

me

version 9

User manual (FreePascal version)

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1. Program versions

The multiple-Einstein program is available as source code written either in Fortran or in FreePascal. These codes are freeware and may be changed and incorporated in different software at your taste. Updates of these codes are available at: <http://www.geo.uu.nl/~jacobs/Downloads>.

The method used in these programs is suitable to construct thermodynamic databases of multi-component systems for application in large ranges of pressure and temperature. Because the calculation of thermodynamic properties in such systems requires efficient high-speed computational techniques, the treatment of physical details of static, vibrational and electronic effects in the programs is necessarily kept simple. The method is detailed in Jacobs et al. (2013) and it is based on representing the vibrational density of states of a substance with multiple Einstein frequencies. The method is semi-empirical, and model parameters were obtained by an inversion technique by a separate program. Although the method lacks the rigor of a complete lattice dynamics theory, we showed in Jacobs et al. (2017), that experimental data are represented with engineering precision.

Many equations are given in this manual, which seems superfluous. They are intended for programming and serve as a check of the code. The source code refers to these equations, making extensions to the program easier.

1.1. FreePascal code

The FreePascal source of the multiple-Einstein program, **me**, is based on simplified procedures and functions of program *XiPT*, which has been employed for carrying out thermodynamic analyses of experimental data. *XiPT* contains an optimizer which established the model parameters of the multiple-Einstein description of each substance given in this manual. The input files for *XiPT* are more complicated relative to those for the multiple-Einstein program, **me**, mainly because of the large number of phases and thermodynamic models that can be treated. To avoid time-sinks in addressing problems with the input, raised by users, program *XiPT* is only very sparsely distributed, until a good manual is available. Instead we follow the idea of copying the most successful models, present in *XiPT*, into a new program, which is called the multiple-Einstein program, **me**. Because the input for that program is much simpler, our work will be more transparent to other investigators. An additional advantage is that the code is easier incorporated into other open thermodynamic software, such as in OpenCalphad (see www.opencalphad.com).

The main unit '**me.pas**' of the FreePascal code shows thermodynamic models that are incorporated in the source code, including a To-Do list of features that will be programmed in the future.

1.2. Fortran code

The Fortran code is based on thermodynamic expressions of the multiple-Einstein method given by Jacobs et al (2013). The routines and functions were programmed independently from the *XiPT* code, serving as a check of *XiPT* itself. Constructing software code in Fortran, starting from the original mathematical expressions of models, consumes more time relative to the copy-paste method used in the FreePascal code. Therefore a time-lag may be expected before the same features as in the FreePascal code are available.

2. Installation

The multiple-Einstein program, *me*, runs in the linux environment of Ubuntu or it may be run in Windows. Executables of *me* are included, but if they do not run, FreePascal is needed to compile the source code.

In Linux:

A. Install FreePascal.

You can use the software manager, or alternatively:

1. Open a terminal window by pressing simultaneously:
cntrl-alt-t
2. At the command prompt in the terminal window type:
sudo apt-get install fp-compiler

B. Install program '*me*':

3. Open a terminal in Ubuntu by pressing simultaneously:
cntrl-alt-t
4. Unpack me.tgz in the directory of your choice and type at the command prompt:
tar -zxf me.tgz
5. Compile the program by typing:
fpc me.pas
6. Run the program by typing:
./me mgo.mef

In Windows

A. Install FreePascal:

1. Download FreePascal from <https://www.freepascal.org>:
fpc-3.04.i386-win32.cross.x86_64-win64.exe and fpc-3.04.i386-win32.exe
2. Execute both programs

B. Install program '*me*':

3. Open a powershell window (windows10) or command prompt (windows7)
4. Unzip me.zip in the directory of your choice by typing:
unzip me.zip
5. Compile the program by typing:
fpc me.pas
6. Run the program by typing:
.\me mgo.mef

An example of how to use '*me*' is given in section 4.

3. Substances in file demo.mef

Substances in file **demo.mef** are given in Table 3.1. A thermodynamic analysis of orthoenstatite, forsterite and platinum is given by Jacobs et al. (2013). The description for periclase (MgO) is a simplification of that by Jacobs et al. (2017) treating substances in the system MgO-SiO₂. The description for periclase allows calculating the shear modulus.

Table 3.1. Nomenclature and structure of substances in demonstration file demo.mef

Formula	Name	Abbreviation	Number of Einstein temperatures	Structure
MgO	periclase	pc	5	<i>Fm3m</i>
Mg ₂ SiO ₄	forsterite	fo	60	<i>Pbnm</i>
MgSiO ₃	orthoenstatite	oen	60	<i>Pbca</i>
Al	aluminium	Al	30	<i>Fm3m</i>
Pt	platinum	Pt	30	<i>Fm3m</i>

4. Using FreePascal program '*me*' to calculate thermodynamic properties

The central equation of the multiple-Einstein method programmed in '*me*' is the Helmholtz energy, and it is partitioned in static lattice, vibrational, electronic, magnetic and defect contributions:

$$A(T,V) = U^{ref} + U^{static}(V) + A^{vib}(T,V) + A^{cf-el}(T) + A^{\lambda}(T) + A^{defect}(T,V) \quad (4.1)$$

The reference energy, U^{ref} in Eq. (4.1), is a constant, and determined by e.g. available heats of formation of the substances or phase boundary data. The second term represents the static lattice energy for a substance in which vibrational motions are absent. This contribution is determined by the equation of state, such as expressions of Birch-Murnaghan (1952), Vinet et al (1987, 1989), or Keane's (1954) equation of state. Expressions for the static lattice contribution to thermodynamic properties are given in the next chapter. Vibrational motions are represented by the third term in Eq. (4.1). The fourth term in Eq. (1) deals with electronic contributions, such as the crystal-field electronic contribution in fayalite Fe_2SiO_4 , described in Jacobs et al (2019) to represent the heat capacity below 100 K. The fifth term in Eq. (1) represents the magnetic contribution, which is e.g. applicable to specific modifications of $FeSiO_3$ and Fe_2SiO_4 . The last term gives a contribution to thermodynamic properties due to defects in the crystal. The mathematical expressions for these terms are detailed by Jacobs et al. (2013, 2017, 2019) and some extensions are given in this manual in chapters 6 - 14.

The input file, **demo.mef**, contains data that can be used in the multiple-Einstein program, *me*. On website <http://www.geo.uu.nl/~jacobs/Downloads>, more examples in the form of databases are present. Program '*me*' calculates thermodynamic properties, including shear modulus for a pure substance, such as for MgO. The output of '*me*' is stored in a table containing these properties on a pressure-temperature grid. To enable to start quickly with '*me*' an example is given below.

Example:

Calculate thermodynamic properties of MgO between 0 and 3000 K with steps of 500 K and between 0 and 20 GPa with steps of 10 GPa. Use a 5-Einstein model.

To construct a table with thermodynamic properties we follow the 5 steps described below:

1. Select the description of MgO given in section 3, Table 3.1, given in file **demo.mef**.
2. Copy the data from **demo.mef** and store them on a new file '**mgo.mef**'. File '**mgo.mef**' will look like:

```
# Comment: File mgo.mef with data copied from file demo.mef
#
<MgO-pc> (* Name of the substance *)
40.304000 (* Mass of the substance in gr/mol *)
2.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-6.21124727753588E+005 (* Static lattice energy in J/mol *)
1.12027710146365E-005 (* Volume/m3/mol at zero K and zero Pa *)
1.10725544416607E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
2 (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice
3 (* Order of Birch-Murnaghan EoS of the static lattice *)
1.713650000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
4.185889000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero Pa *)
1.398012000000000E+011 (* Static lattice shear modulus/Pa at zero Pa *)
2.274201000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero Pa *)
2.068608000000000E+000 (* Vibrational parameter of the shear modulus *)
```



```

0 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
0 (* 0=No magnetic contribution, 1=magnetic contribution *)
0 (* No electronic contribution *)
0 (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984)*)
0 (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &...*)
# Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
5 (* Number of Einstein modes *)
2 (* l=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by
Stixrude & Lithgow-Bertelloni, 2005 *)
# j Theta/K Fraction Gamma Mode_m(q) Gamma_inf a0 z
# -----
1 103.6373 8.906551151E-003 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
2 310.9115 1.518128083E-001 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
3 518.1859 4.489913319E-001 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
4 725.4603 3.115346305E-001 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
5 932.7346 7.875467817E-002 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
#
# sum of all fractions: 1.000000000E+000
#####

```

3. Next the pressure-temperature ranges with their steps must be attached to file '**mgo.mef**'.
Go to the last part of file '**demo.mef**' and copy the lines:

```

# Comment: last part of file demo.mef: these lines must be changed manually
# -----
# Isobaric calculation
1 (* 1=Isobaric calculation, 2=Isothermal calculation *)
10 2000 30 (* Temperature range and step: T_start/K, T_end/K, T_step/K *)
1e+05 1e+05 0.0 (* Pressure range and step : P_start/Pa, P_end/Pa, P_step/Pa *)
1 (* Output: 1=Output to screen and file, 0=Output to file only *)
# Output file name
/home/michel/geodata/mgo/mgo.out
# -----
#####

```

4. Insert these lines into file '**mgo.mef**', and change them to the desired ranges of pressure and temperature. The final resulting file '**mgo.mef**' will look like:

```

# Comment: File mgo.mef with data copied from file demo.mef: final result
#
<MgO-pc> (* Name of the substance *)
40.304000 (* Mass of the substance in gr/mol *)
2.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-6.21124727753588E+005 (* Static lattice energy in J/mol *)
1.12027710146365E-005 (* Volume/m3/mol at zero K and zero Pa *)
1.10725544416607E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
2 (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice
3 (* Order of Birch-Murnaghan EoS of the static lattice *)
1.713650000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
4.185889000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero Pa *)
1.398012000000000E+011 (* Static lattice shear modulus/Pa at zero Pa *)
2.274201000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero Pa *)
2.068608000000000E+000 (* Vibrational parameter of the shear modulus *)
0 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
0 (* 0=No magnetic contribution, 1=magnetic contribution *)
0 (* No electronic contribution *)
0 (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984)*)
0 (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &...*)
# Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
5 (* Number of Einstein modes *)
2 (* l=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by
Stixrude & Lithgow-Bertelloni, 2005 *)
# j Theta/K Fraction Gamma Mode_m(q) Gamma_inf a0 z
# -----
1 103.6373 8.906551151E-003 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
2 310.9115 1.518128083E-001 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
3 518.1859 4.489913319E-001 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
4 725.4603 3.115346305E-001 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
5 932.7346 7.875467817E-002 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
#

```

```

# sum of all fractions: 1.000000000E+000
#####
# Comment: last part of file demo.mef: these lines are now changed manually
# -----
# Isobaric calculation
1 (* 1=Isobaric calculation, 2=Isothermal calculation *)
0 3000 500 (* Temperature range and step: T_start/K, T_end/K, T_step/K *)
0 20e+09 10e+09 (* Pressure range and step : P_start/Pa, P_end/Pa, P_step/Pa *)
1 (* Output: 1=Output to screen and file, 0=Output to file only *)
# Output file name
/home/michel/programs/me/mgo.out
# -----
#####

```

5. The table of thermodynamic properties is constructed by calling the multiple-Einstein program **'me'** with the input file as argument.

- Open a terminal in Ubuntu by pressing simultaneously: cntrl-alt-t.
(Alternatively in Windows: open powershell or command prompt)
- Go to the directory where program **'me'** is present
- When file **'mgo.mef'** is present in the same directory as program **'me'** type:
./me mgo.mef
(Alternatively in Windows powerhell: .\me mgo.mef)
- The output file is created in the desired directory.

5. Static contributions

5.1. n^{th} order Birch-Murnaghan equation of state

We follow Stixrude and Lithgow-Bertelloni (2005) for expressing Helmholtz energy and elastic constants in Eulerian finite strain, ' f '. Some details are also given by Anderson (1998). We denote the order of Equation of State by ' n ', which is the largest exponent of strain in the Helmholtz energy.

$$\text{Helmholtz energy: } A^{\text{static}}(f) = V_0^{\text{static}} \sum_{v=2}^n \left(a_v \frac{f^v}{v!} \right) \quad (5.1)$$

$$\text{Pressure: } P^{\text{static}}(f) = \frac{1}{3} (1+2f)^{5/2} \sum_{v=2}^n \left(a_v \frac{f^{v-1}}{(v-1)!} \right) \quad (5.2)$$

$$\text{Bulk modulus: } K^{\text{static}}(f) = \frac{1}{9} (1+2f)^{5/2} \left\{ 5 \sum_{v=2}^n \left(a_v \frac{f^{v-1}}{(v-1)!} \right) + (1+2f) \sum_{v=2}^n \left(a_v \frac{f^{v-2}}{(v-2)!} \right) \right\} \quad (5.3)$$

$$\text{Shear modulus: } G_{\text{shear}}^{\text{static}} = (1+2f)^{5/2} \sum_{v=2}^n \left\{ \left[b_v + \left(2b_v + \frac{a_v}{3(v-1)} \right) f \right] \frac{f^{v-2}}{(v-2)!} \right\} \quad (5.4)$$

$$\text{Strain: } f = \frac{1}{2} \left[\left(\frac{V}{V_0^{\text{static}}} \right)^{-2/3} - 1 \right] \quad (5.5)$$

Table 5.1 shows to 4th order in strain, relations between the coefficients in eqn. (5.1) - (5.4) and bulk modulus, shear modulus and their pressure derivatives at the static volume, V_0^{static} . V_0^{static} is the volume of the static lattice in which no vibrational motion is present, at zero static pressure.

Table 5.1. Relation between coefficients in the expressions (5.1) and (5.2) and static properties to fourth order in strain in the expression for Helmholtz free energy. The coefficients apply at zero static pressure, at which the volume equals V_0^{static} . Temperature is not defined in a static lattice.

EoS order	v	a_v	b_v
2	2	$9K_0^{\text{st}}$	G_0^{st}
3	3	$27K_0^{\text{st}}(K_0^{\prime\text{st}} - 4)$	$3K_0^{\text{st}}(G_0^{\prime\text{st}} - 1) - 7G_0^{\text{st}}$
4	4	$81K_0^{\text{st}} \left[K_0^{\text{st}} K_0^{\prime\text{st}} + K_0^{\prime\text{st}} (K_0^{\prime\text{st}} - 7) + \frac{143}{9} \right]$	$9(K_0^{\text{st}})^2 G_0^{\prime\text{st}} + 3K_0^{\text{st}} (G_0^{\prime\text{st}} - 1) (3K_0^{\prime\text{st}} - 16) + 63G_0^{\text{st}}$

$$K_0^{\prime\text{st}} = \left(\frac{\partial K^{\text{static}}}{\partial P} \right)_{f=0}, K_0^{\prime\prime\text{st}} = \left(\frac{\partial^2 K^{\text{static}}}{\partial P^2} \right)_{f=0}, G_0^{\prime\text{st}} = \left(\frac{\partial G^{\text{static}}}{\partial P} \right)_{f=0}, G_0^{\prime\prime\text{st}} = \left(\frac{\partial^2 G^{\text{static}}}{\partial P^2} \right)_{f=0}$$

Values for the coefficients a_v and b_v are quite large. To represent the curvature in bulk modulus of orthoenstatite one obtains values comparable to, $a_2 = 1.069 \times 10^{12}$ Pa, $a_3 = 1.111 \times 10^{13}$ Pa, and $a_4 = -3.125 \times 10^{14}$ Pa. Computations using an optimizer, such as present in *XiPT*, are more efficient when use is made of smaller values of coefficients. In that case one is able to keep track on the evolution of the values for static bulk and shear modulus at 0 Kelvin and 0 Pa, K_0^{static} and G_0^{static} . Expression

(5.1) – (5.3) are rewritten in terms of K_0^{static} by defining coefficient x_v and inserting it in these expressions:

$$x_v = \frac{a_v}{9K_0^{static} (v-1)!} \quad v \geq 2 \quad (5.6)$$

$$A^{static}(f) = 9K_0^{static} V_0^{static} \sum_{v=2}^n \frac{x_v f^v}{v} \quad (5.7)$$

$$P^{static}(f) = 3K_0^{static} (1+2f)^{5/2} \sum_{v=2}^n x_v f^{v-1} \quad (5.8)$$

$$K^{static}(f) = K_0^{static} (1+2f)^{5/2} \left\{ 5 \sum_{v=2}^n x_v f^{v-1} + (1+2f) \sum_{v=2}^n x_v \cdot (v-1) \cdot f^{v-2} \right\} \quad (5.9)$$

Values for coefficients x_v are smaller than for a_v and dimensionless: for orthoenstatite, $x_2 = 1$, $x_3 = 5.20$, $x_4 = -48.7$. Apart from that, K_0^{static} instead of a_2 is a fitting variable. Because $x_2 = 1$ only values for $v \geq 3$ are written in the input file of **'me'**. Table 5.2 gives relations between bulk modulus and its pressure derivatives and coefficients x_v .

*When use is made of the Birch-Murnaghan equation of state and the order of the equation of state is larger than 3, values for K_0^{static} and x_v ($v \geq 3$) are given in the input file of **'me'**. If the order of the equation of state is 3, values for K_0^{static} and its pressure derivative, $(K_0^{static})'$, are given in the input file.*

To keep track on the evolution of static shear modulus in an optimizer, and to obtain smaller values for shear modulus coefficients, we insert eqn. (5.6) into eqn. (5.4). Additionally we use the coefficient y_v and rewrite (5.4) to:

$$G_{shear}^{static}(f) = (1+2f)^{7/2} G_0^{static} \sum_{v=2}^n y_v f^{v-2} + 3K_0^{static} (1+2f)^{5/2} \sum_{v=2}^n x_v f^{v-1} \quad (5.10)$$

$$y_v = \frac{b_v}{G_0^{static} (v-2)!} \quad v \geq 2 \quad (5.11)$$

Note that the last term in eqn. (5.10) is the same expression as for the static pressure, eqn. (5.8). Because $y_2 = 1$ only values for $v \geq 3$ are written in the input file of **'me'**.

*When use is made of the Birch-Murnaghan equation of state and the order of the equation of state is larger than 3, values for G_0^{static} and y_v ($v \geq 3$) are given in the input file of **'me'**. If the order of the equation of state is 3, values for G_0^{static} and its pressure derivative, $(G_0^{static})'$, are given in the input file.*

Table 5.2. Relation between coefficients in the expressions (5.7) - (5.10) and static properties to fourth order in strain in the expression for Helmholtz free energy. The coefficients apply at zero static pressure at which the volume equals V_0^{static} .

EoS order	ν	x_ν	y_ν
2	2	1	1
3	3	$\frac{3}{2}(K_0'^{st} - 4)$	$\frac{3K_0^{st}(G_0'^{st} - 1)}{G_0^{st}} - 7$
4	4	$\frac{3}{2}\left[K_0^{st}K_0''^{st} + K_0'^{st}(K_0'^{st} - 7) + \frac{143}{9}\right]$	$\frac{9(K_0^{st})^2 G_0''^{st} + 3K_0^{st}(G_0'^{st} - 1)(3K_0'^{st} - 16) + 63G_0^{st}}{2G_0^{st}}$

5.2. Example input file:

Part of an input file for MgSiO₃ orthoenstatite. Pressure derivative coefficients, x_ν and y_ν are on the blue coloured lines below. From Table 5.2: $K_0'^{st} = 7.4644$, $K_0''^{st} = -0.4361 \text{ GPa}^{-1}$,

$$G_0'^{st} = 1.5022, \quad G_0''^{st} = -0.2056 \text{ GPa}^{-1}$$

```

<MgSiO3-oen>          (* Name of the substance *)
100.388000            (* Mass of the substance in gr/mol *)
5.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-1.60212051918842E+006 (* Static lattice energy in J/mol *)
3.12229309698018E-005 (* Volume/m3/mol at zero K and zero Pa *)
3.08364030030436E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
2                    (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice *)
4                    (* Order of Birch-Murnaghan EoS of the static lattice *)
1.188277000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
5.196620000000000E+000 (* --- 1st pressure derivative coefficient of the static lattice bulk mod
-4.870380000000000E+001 (* --- 2nd pressure derivative coefficient of the static lattice bulk mod
8.320004000000000E+010 (* Static lattice shear modulus/Pa at zero Pa *)
-4.848273000000000E+000 (* --- 1st pressure derivative coefficient of the static lattice shear mod
-1.186525000000000E+002 (* --- 2nd pressure derivative coefficient of the static lattice shear mod
1.690556000000000E+000 (* Vibrational parameter of the shear modulus *)
0                    (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
0                    (* 0=No magnetic contribution, 1=magnetic contribution *)
0                    (* No electronic contribution *)
0                    (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984) *)
0                    (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &...*)
# Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
60                   (* Number of Einstein modes *)
:
:

```

5.3. Vinet's Equation of state

The expressions of static Helmholtz energy, pressure and bulk modulus belonging to the 3rd order Equation of State by Vinet (1987,1989) are given below:

$$A^{st}(V) = \frac{4K_0^{st}V_0^{st}}{(K_0'^{st} - 1)^2} \left\{ 1 + \left[\frac{3}{2}(K_0'^{st} - 1)f - 1 \right] \exp \left[\frac{3}{2}(K_0'^{st} - 1)f \right] \right\} \quad K_0'^{st} \neq 1 \quad (5.12)$$

$$A^{st}(V) = 9K_0^{st}V_0^{st} \left(\frac{1}{2}f^2 - \frac{1}{3}f^3 \right) \quad K_0'^{st} = 1 \quad (5.13)$$

$$P^{st}(V) = 3K_0^{st} \frac{f}{(1-f)^2} \exp \left\{ \frac{3}{2}(K_0'^{st} - 1)f \right\} \quad (5.14)$$

$$K^{st}(V) = K_0^{st} \left\{ \frac{1+f}{(1-f)^2} + \frac{3}{2} \left(K_0^{st} - 1 \right) \frac{f}{1-f} \right\} \exp \left\{ \frac{3}{2} \left(K_0^{st} - 1 \right) f \right\} \quad (5.15)$$

$$f = 1 - \left(\frac{V}{V_0^{st}} \right)^{1/3} \quad (5.16)$$

Eqn. (2.8) illustrates that the Helmholtz energy is zero when the volume equals the static volume at zero pressure, V_0^{st} . For large volume Helmholtz energy behaves asymptotically:

$$\lim_{V \rightarrow \infty} A^{st}(V) = \frac{4K_0^{st}V_0^{st}}{\left(K_0^{st} - 1\right)^2} \quad (5.17)$$

5.4. Keane's Equation of State

The expressions of static Helmholtz energy, pressure and bulk modulus belonging to the 3rd order Equation of State by Keane (1954) are given below:

$$A^{st}(V) = -K_0^{st}V_0^{st} \left\{ \frac{K_0^{st}}{\left(K_\infty^{st}\right)^2} \left[\frac{\eta^{1-K_\infty^{st}} - 1}{1 - K_\infty^{st}} + 1 - \eta \right] + \left(\frac{K_0^{st}}{K_\infty^{st}} - 1 \right) [\eta \ln \eta + 1 - \eta] \right\} \quad K_\infty^{st} \neq 1 \quad (5.18a)$$

$$A^{st}(V) = -K_0^{st}V_0^{st} \left\{ K_0^{st} [\ln(\eta) - \eta + 1] + \left(K_0^{st} - 1 \right) [\eta \ln(\eta) - \eta + 1] \right\} \quad K_\infty^{st} = 1 \quad (5.18b)$$

$$P^{st}(V) = K_0^{st} \left\{ \frac{K_0^{st} \left(\eta^{-K_\infty^{st}} - 1 \right)}{\left(K_\infty^{st}\right)^2} + \left(\frac{K_0^{st}}{K_\infty^{st}} - 1 \right) \ln(\eta) \right\} \quad (5.19)$$

$$K^{st}(V) = K_0^{st} \left\{ \frac{K_0^{st}}{K_\infty^{st}} \left(\eta^{-K_\infty^{st}} - 1 \right) + 1 \right\} \quad (5.20)$$

$$\eta = \frac{V}{V_0^{st}} \quad (5.21)$$

The parameter K_0^{st} is the pressure derivative of bulk modulus at zero pressure, whereas K_∞^{st} is the pressure derivative of isothermal bulk modulus at infinite pressure.

Jacobs et al (2013) showed for Aluminium, that Keane's Equation of State has the advantage that shock-wave-reduced data and ab-initio predictions up to 1000 GPa can be accurately represented, whereas that was not possible with a 4th order Birch-Murnaghan Equation of State. The description for Aluminium employing Keane's (1954) EoS is present in file [demo.mef](#).

A part of the input file is given below, with the relevant lines in blue.

```
<Al-30E-Keane>          (* Name of the substance *)
40.304000                (* Mass of the substance in gr/mol *)
1.0000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-8.33195291982642E+003  (* Static lattice energy in J/mol *)
9.87223791700162E-006  (* Volume/m3/mol at zero K and zero Pa *)
9.77267467875569E-006  (* Volume/m3/mol of the static lattice at zero Pa *)
3                        (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice *)
4                        (* Order of Keane EoS static of the lattice *)
8.184978000000000E+010 (* Static lattice bulk modulus/Pa at zero Pa *)
```

```

5.020000000000000E+000      (* Pressure derivative of the static lattice bulk modulus at zero Pa *)
2.340000000000000E+000      (* Pressure derivative of the static lattice bulk modulus at infinite...
0                             (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
0                             (* 0=No magnetic contribution, 1=magnetic contribution *)
1                             (* Free electron gas model *)
# Cv=a*T*(V/V0)^gamma_el
6.666667000000000E-001      (* Electronic Gruneisen parameter, gamma_el *)
1.350000000000000E-003      (* Electronic coefficient, a, in J/mol/K/K *)
0                             (* 0=No cation disorder, 1=cation disorder: model of O'Neill and Navr
0                             (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets & Oga
# Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
30                            (* Number of Einstein modes *)
1                             (* 1=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by Stix
# j   Theta/K   Fraction   Gamma   Mode_m(q)   Gamma_inf   a0   z
# -----
1     12.696713  0.000000000E+000  2.1400000  2.0100000  0.7400000  0.000000E+000  0.0000000
2     29.113019  2.900029000E-004  2.1400000  2.0100000  0.7400000  0.000000E+000  0.0000000
3     45.530759  9.700097001E-004  2.1400000  2.0100000  0.7400000  0.000000E+000  0.0000000
4     61.948499  1.870018700E-003  2.1400000  2.0100000  0.7400000  0.000000E+000  0.0000000
5     78.366239  3.220032200E-003  2.1400000  2.0100000  0.7400000  0.000000E+000  0.0000000
.     .         .         .         .         .         .         .
.     .         .         .         .         .         .         .

```

5.5. Equation of state by Qin (2008)

The n -th order Birch-Murnaghan and n -th order Vinet EoS may result in problems with convergence of the energy at very large or very small volumes for n larger than 3. Relative to a n -th order Birch-Murnaghan EoS, a n -th order Vinet EoS is characterized by the feature that the Helmholtz energy cannot be written as an analytical function.

To overcome these problems, Qin et al. (2008) developed a new equation of state which they tested on transition metals using DFT. The equation of state contains apart from V_0^{st} and K_0^{st} , four other parameters p , q , m , n . The average static potential between the atoms in the crystal shows the correct asymptotical behavior at large volumes.

Expressions for Helmholtz energy, pressure and bulk modulus are given below.

Helmholtz energy

$$A^{st}(V) = \frac{9K_0^{st}V_0^{st}(q-n)}{(p+m)(q-n)[(p+m)-(q-n)]+pn+qm} \left\{ \frac{e^{-p(x-1)}}{x^m} - 1 - \frac{p+m}{q-n} \left(x^n e^{-q(x-1)} - 1 \right) \right\} \quad (5.22)$$

$$x = \left(\frac{V}{V_0^{st}} \right)^{1/3}, \quad (n, m \geq 0)$$

The Helmholtz energy is written such that it is zero at $x=1$. At infinite volume the Helmholtz energy has the asymptotic value:

$$A^{st}(x \rightarrow \infty) = \frac{9K_0^{st}V_0^{st}(q-n)}{(p+m)(q-n)[(p+m)-(q-n)]+pn+qm} \left\{ -1 + \frac{p+m}{q-n} \right\} \quad (5.23)$$

Pressure

$$P^{st}(V) = \frac{3K_0^{st} \left\{ (q-n)x^{-m} \left(p + \frac{m}{x} \right) e^{-p(x-1)} - (p+m)x^n \left(q - \frac{n}{x} \right) e^{-q(x-1)} \right\}}{x^2 \left\{ (p+m)(q-n)[(p+m)-(q-n)]+pn+qm \right\}} \quad (5.24)$$

Bulk modulus

$$K^{st}(V) = \frac{K_0^{st}}{(p+m)(q-n)[(p+m)-(q-n)] + pn + qm} \times \left\{ (q-n)x^{-m-1}e^{-p(x-1)} \left[m(m+3)x^{-2} + 2p(m+1)x^{-1} + p^2 \right] + (p+m)x^{n-1}e^{-q(x-1)} \left[-n(n-3)x^{-2} + 2q(n-1)x^{-1} - q^2 \right] \right\} \quad (5.25)$$

The equation of state by Qin et al (2008) is a good alternative for a 4th order Vinet equation of state. In Jacobs et al (2010, 2013) a multiple-Einstein model is given that accurately represents the thermodynamic properties of aluminium. In these works it was shown that the equation of state by Keane (1954) performs better than a 3rd order Vinet and 4th order Birch-Murnaghan equation of state. It turns out that models employing the equation of state by Qin et al (2008) and a 5th order Birch-murnaghan perform equally well as a Keane equation of state. These models are included in file [demo.mef](#). In Figure 5.1 some results are given compared to experimental data and with synthetic data calculated with the model employing Keane's (1954) equation of state. A part of the input file is given below.

```
#
<Al-30E-Qin> (* Name of the substance *)
40.304000 (* Mass of the substance in gr/mol *)
1.0000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-8.33195291982642E+003 (* Static lattice energy in J/mol *)
9.87507532890812E-006 (* Volume/m3/mol at zero K and zero Pa *)
9.77821726967774E-006 (* Volume/m3/mol of the static lattice at zero Pa *)
4 (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static latti*)
4 (* Order of Qin et al (2008) EoS of the static lattice *)
8.1769340000000000E+010 (* Static lattice bulk modulus/Pa at zero Pa *)
5.2548030000000000E+000 (* Coefficient "p" in the EoS of Qin et al 2008 *)
5.3698090000000000E+000 (* Coefficient "q" in the EoS of Qin et al 2008 *)
0 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
0 (* 0=No magnetic contribution, 1=magnetic contribution *)
1 (* Free electron gas model *)
# Cv=a*T*(V/V0)^gamma_el
6.6666670000000000E-001 (* Electronic Gruneisen parameter, gamma_el *)
1.3500000000000000E-003 (* Electronic coefficient, a, in J/mol/K/K *)
0 (* 0=No cation disorder, 1=cation disorder: model of O'Neill and
Navrotsky (1983,1984) *)
0 (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &
Oganov 2007 Phys Rev B 75:024115 *)
# Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
30 (* Number of Einstein modes *)
1 (* 1=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by
Stixrude & Lithgow-Bertelloni, 2005 *)
# j Theta/K Fraction Gamma Mode_m(q) Gamma_inf a0 z
# -----
1 12.696713 0.0000000000E+000 2.0860910 4.2699600 1.1924480 0.000000E+000 0.0000000
2 29.113019 2.9000290000E-004 2.0860910 4.2699600 1.1924480 0.000000E+000 0.0000000
3 45.530759 9.700097001E-004 2.0860910 4.2699600 1.1924480 0.000000E+000 0.0000000
4 61.948499 1.870018700E-003 2.0860910 4.2699600 1.1924480 0.000000E+000 0.0000000
5 78.366239 3.220032200E-003 2.0860910 4.2699600 1.1924480 0.000000E+000 0.0000000
```

If parameters m and n are needed, the order of the EoS is 6, and the file should be extended as:

```
9.77821726967774E-006 (* Volume/m3/mol of the static lattice at zero Pa *)
4 (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static latti*)
6 (* Order of Qin et al (2008) EoS of the static lattice *)
8.1769340000000000E+010 (* Static lattice bulk modulus/Pa at zero Pa *)
5.2548030000000000E+000 (* Coefficient "p" in the EoS of Qin et al 2008 *)
5.3698090000000000E+000 (* Coefficient "q" in the EoS of Qin et al 2008 *)
1.0000000000000000E-009 (* Coefficient "m" in the EoS of Qin et al 2008 *)
1.0000000000000000E-009 (* Coefficient "n" in the EoS of Qin et al 2008 *)
```

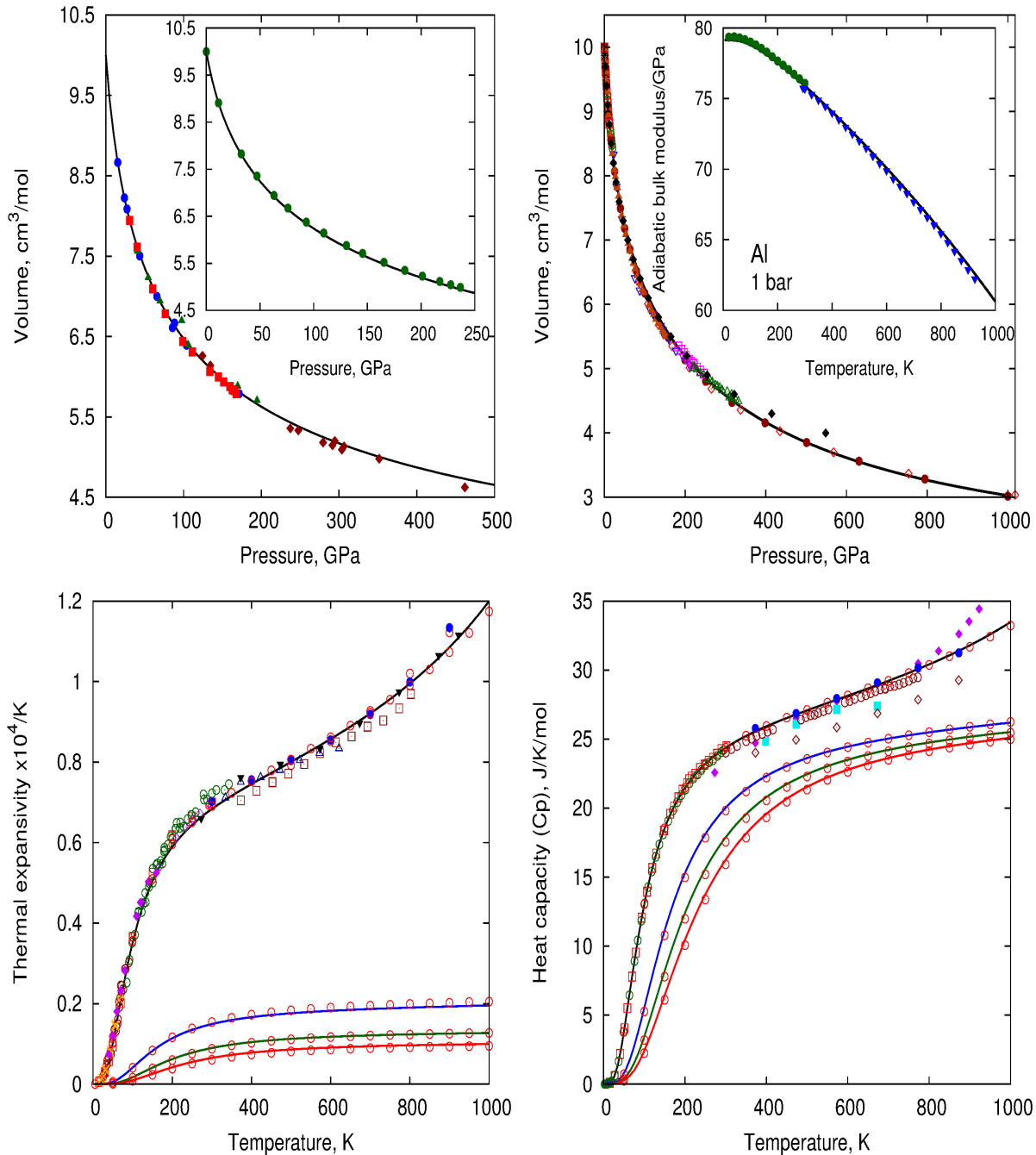



Fig. 5.1. Calculations for Aluminium given as solid lines were performed employing Qin et al's (2008) equation of state for the static lattice (see file [demo.mef](#)). **Top-left:** Hugoniot with an isentrope with entropy 28.3 J/K/mol as inset. Melting on the Hugoniot takes place at about 135 GPa. Experimental data above that pressure are valid for liquid aluminium. These data were not taken into account in the optimization process of all experimental data. Examples of how to calculate Hugoniots and isentropes are given in chapter 17. **Top-right:** Volume-Pressure curve at 298 K and 1-bar adiabatic bulk modulus as inset. **Bottom-left:** Thermal expansivity at 1 bar (black), 50 GPa (blue), 100 GPa (green), 150 GPa (red). Open circles are synthetic data calculated with a model employing Keane's (1954) EoS. **Bottom-right:** heat capacity at 1 bar (black), 50 GPa (blue), 100 GPa (green), 150 GPa (red). Open circles are synthetic data calculated with a model employing Keane's (1954) EoS. Experimental data are given in Jacobs et al (2010, 2013) and in Jacobs & Oonk (2012)

6. Vibrational contributions

The vibrational formalism is based on that described by Jacobs et al. (2013). Here we summarize the equations used in program **'me'**. In the method the VDoS is described with N_E Einstein frequencies. To make the equations shorter we make use of the expressions:

$$x_j = \frac{h\nu_j}{kT} = \frac{\theta_j}{T} \quad (6.1)$$

In eqn. (6.1) the j^{th} Einstein frequency is represented by ν_j , the j^{th} Einstein temperature by θ_j , temperature by T , h is Planck's constant and k Boltzmann's constant. This section gives expressions for the Helmholtz energy, A , entropy, S , isochoric heat capacity, C_V , pressure, P , its isochoric temperature derivative, $(\partial P/\partial T)_V$ and isothermal bulk modulus, K . The vibrational contribution to Helmholtz energy is composed of a quasi-harmonic and anharmonic part. For the anharmonic part we use the perturbation formalism of Oganov and Dorogokupets (2003). The Helmholtz energy contribution of the j^{th} frequency for a 1 mole of substance with n atoms in the molecular formula unit is given by:

$$A_j^{\text{vib}} = A_{qhm,j}^{\text{vib}} + A_{anh,j}^{\text{vib}} = 3nRT \left\{ \frac{x_j}{2} + \ln(1 - e^{-x_j}) \right\} + \frac{3nRT^2 a_j}{6} \left[\frac{1}{4} x_j^2 + \frac{3x_j^2 e^{x_j}}{(e^{x_j} - 1)^2} \right] \quad (6.2)$$

When the complete VDoS is considered, the total vibrational contribution to Helmholtz energy is written in terms of the weight or fraction in which the j^{th} frequency appears in the VDoS.

$$A^{\text{vib}} = 3nRT \sum_{j=1}^{N_E} \left\{ f_j \left[\frac{x_j}{2} + \ln(1 - e^{-x_j}) \right] \right\} + \frac{3nRT^2}{6} \sum_{j=1}^{N_E} \left\{ a_j f_j \left[\frac{1}{4} x_j^2 + \frac{3x_j^2 e^{x_j}}{(e^{x_j} - 1)^2} \right] \right\} \quad (6.3)$$

The total contributions are given by Jacobs et al. (2013). Program **'me'** mostly uses Einstein expressions for a single frequency, which are then summed in procedures **thermal_pressure()** and **single_vibration_property()** of unit **vibrations.pas**. Therefore, we give expressions for a single Einstein frequency below. We retain the index j in the expressions, indicating that they appear in a summation.

6.1. Grüneisen parameters, vibrational contribution to shear modulus

Einstein frequencies used in eqn. (6.3) are volume dependent, and not temperature dependent. In **'me'** two expressions can be defined for the volume dependence of frequencies.

A. The expressions by Alt'shuler et al. (1987) are in terms of x_j . The Grüneisen parameter is given by:

$$\gamma_j = \gamma_{j,\infty} + (\gamma_{j,0} - \gamma_{j,\infty}) \left(\frac{V}{V_0} \right)^{m_j} \quad (6.4)$$

With the definition for Grüneisen parameter, the frequencies are obtained.

$$\gamma_j = - \left(\frac{\partial \ln x_j}{\partial \ln V} \right)_T \quad (6.5)$$

$$- \left(\frac{\partial \gamma_j}{\partial V} \right)_V = -\gamma_j q_j = -m_j (\gamma_{j,0} - \gamma_{j,\infty}) \left(\frac{V}{V_0} \right)^{m_j} \quad (6.6)$$

$$\ln \left(\frac{x_j}{x_{j,0}} \right) = -\gamma_{j,\infty} \ln \left(\frac{V}{V_0} \right) - \frac{\gamma_{j,0} - \gamma_{j,\infty}}{m_j} \left[\left(\frac{V}{V_0} \right)^{m_j} - 1 \right] \quad \text{and } m_j \neq 0 \quad (6.7)$$

$$\ln \left(\frac{x_j}{x_{j,0}} \right) = -\gamma_{j,0} \ln \left(\frac{V}{V_0} \right) \quad \text{and } m_j = 0 \quad (6.8)$$

The subscript '0' in eqn. (6.4-6.8) and refers to the zero temperature and zero pressure condition. The Grüneisen parameter at infinite pressure is defined by γ_∞ .

B. The expressions used by Stixrude and Lithgow-Bertelloni (2005) are:

$$(x_j)^2 = (x_{j,0})^2 \left(1 + a_{ii,j}^{(1)} \varphi + \frac{1}{2} a_{iikk,j}^{(2)} \varphi^2 + \dots \right) \quad (6.9)$$

In eqn. (6.9) the isotropic strain, φ , is given by:

$$\varphi = \frac{1}{2} \left[\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right] \quad (6.10)$$

From the definition of the Grüneisen parameter we find:

$$\gamma_j = \left(\frac{\partial \ln x_j}{\partial \ln V} \right)_T = \frac{1}{6} \left(\frac{x_{j,0}}{x_j} \right)^2 (2\varphi + 1) (a_{ii,j}^{(1)} + a_{iikk,j}^{(2)} \varphi) \quad (6.11)$$

$$-V \left(\frac{\partial \gamma_j}{\partial V} \right)_T = -\gamma_j q_j = -\frac{1}{9} \left(18\gamma_j^2 - 6\gamma_j - \frac{1}{2} \left(\frac{x_{j,0}}{x_j} \right)^2 (2\varphi + 1)^2 a_{iikk,j}^{(2)} \right) \quad (6.12)$$

Grüneisen parameters appear in the expressions of vibrational contribution to pressure, its temperature derivative at constant volume and bulk modulus. The property given by eqn. (6.12) appears only in bulk modulus.

The coefficients $a_{ii,j}^{(1)}$ and $a_{iikk,j}^{(2)}$ are related to the Grüneisen parameters and mode- q parameters as:

$$a_{ii,j}^{(1)} = 6\gamma_{j,0} \quad (6.13)$$

$$a_{iikk,j}^{(2)} = -12\gamma_{j,0} + 36\gamma_{j,0}^2 - 18\gamma_{j,0} q_{j,0} \quad (6.14)$$

This formalism enables treatment of the elastic constants and shear modulus. Shear modulus is:

$$G_{shear}^{vib}(T, V) = -\frac{3nRT}{V} \sum_{j=1}^{N_E} n_{s,j} f_j x_j \left(\frac{1}{2} + \frac{1}{e^{x_j} - 1} \right) \quad (6.15)$$

The shear strain derivatives $n_{s,j}$ appear in the shear modulus contribution are given by:

$$n_{s,j} = -\gamma_j + \left(\frac{x_j}{x_{j,0}} \right)^2 (2\varphi + 1)^2 (\gamma_{j,0} + n_{s,j,0}) \quad (6.16)$$

6.2. Intrinsic anharmonicity

Expressing thermal pressure, its isochoric temperature derivative and bulk modulus, requires volume derivatives of intrinsic anharmonicity, a_j , defined as:

$$a_j = \left(\frac{\partial \ln v_j}{\partial T} \right)_V \quad (6.17)$$

We follow Oganov and Dorogokupets (2003) by writing for the anharmonicity parameter:

$$a_j(V) = a_{0,j} \left(\frac{V}{V_0} \right)^{z_j} \quad (6.18)$$

In (6.18) volume V_0 refers to the real physical volume at zero temperature and zero pressure (not the static lattice volume). The property $a_{0,j}$ is the anharmonicity parameter at zero temperature and zero pressure. The first derivative of the anharmonicity $a_j(V)$ with respect to volume is present in the thermal pressure, its isochoric temperature derivative, and the isothermal bulk modulus. The second derivative with respect to volume is only present in the isothermal bulk modulus. The first and second derivatives are given by:

$$a'_j(V) = \frac{z_j a_{0,j}}{V} \left(\frac{V}{V_0} \right)^{z_j} = \frac{z_j a_j}{V} \quad (6.19)$$

$$a''_j(V) = \frac{z_j a_j}{V^2} (z_j - 1) \quad (6.20)$$

6.3. Thermodynamic contributions

Thermodynamic properties below are expressed for the j^{th} Einstein frequency in the VDoS.

Helmholtz energy

$$A_j^{\text{vib}} = 3nRT \left\{ \frac{x_j}{2} + \ln(1 - e^{-x_j}) \right\} + \frac{3nRT^2 a_j}{6} \left[\frac{1}{4} x_j^2 + \frac{3x_j^2 e^{x_j}}{(e^{x_j} - 1)^2} \right] \quad (6.21a)$$

$$\lim_{x_j \rightarrow \infty} A_{qhm,j}^{\text{vib}} = 3nRT \frac{x_j}{2} = \frac{3}{2} nR\theta_j \quad (6.21b)$$

$$\lim_{x_j \rightarrow 0} A_{qhm,j}^{\text{vib}} = 3nRT \left\{ \frac{x_j}{2} + \ln(x_j) \right\} = 3nR \left\{ \frac{\theta_j}{2} + T \ln \left(\frac{\theta_j}{T} \right) \right\} \quad (6.21c)$$

$$\lim_{x_j \rightarrow \infty} A_{anh,j}^{\text{vib}} = \frac{3nRT^2 a_j}{24} x_j^2 \quad (6.21d)$$

$$\lim_{x_j \rightarrow 0} A_{anh,j}^{vib} = \frac{3}{2} nRT^2 a_j \quad (6.21e)$$

Entropy

$$S_j^{vib} = 3nR \left\{ -\ln(1 - e^{-x_j}) + \frac{x_j}{e^{x_j} - 1} \right\} - \frac{3nRTa_j}{6} \left[\frac{3x_j^3 e^{x_j} (e^{x_j} + 1)}{(e^{x_j} - 1)^3} \right] \quad (6.22a)$$

$$\lim_{x_j \rightarrow \infty} S_{qhm,j}^{vib} = 0 \quad (6.22b)$$

$$\lim_{x_j \rightarrow 0} S_{qhm,j}^{vib} = 3nR(-\ln(x_j) + 1) \quad (6.22c)$$

$$\lim_{x_j \rightarrow \infty} S_{anh,j}^{vib} = 0 \quad (6.22d)$$

$$\lim_{x_j \rightarrow 0} S_{anh,j}^{vib} = -3nRTa_j \quad (6.22e)$$

Energy

$$U_j^{vib} = 3nRT \left\{ \frac{x_j}{2} + \frac{x_j}{e^{x_j} - 1} \right\} + \frac{3nRT^2 a_j}{6} \left\{ \frac{x_j}{4} + \frac{3x_j^2 e^{x_j}}{(e^{x_j} - 1)^2} + \frac{3x_j^3 e^{x_j} (e^{x_j} + 1)}{(e^{x_j} - 1)^3} \right\} \quad (6.23a)$$

$$\lim_{x_j \rightarrow \infty} U_{qhm,j}^{vib} = 3nRT \frac{x_j}{2} \quad (6.23b)$$

$$\lim_{x_j \rightarrow 0} U_{qhm,j}^{vib} = 3nRT \quad (6.23c)$$

$$\lim_{x_j \rightarrow \infty} U_{anh,j}^{vib} = \frac{3nRT^2 a_j}{24} x_j^2 \quad (6.23d)$$

$$\lim_{x_j \rightarrow 0} U_{anh,j}^{vib} = -\frac{3}{2} nRT^2 a_j \quad (6.23e)$$

Isochoric heat capacity

$$C_{V,j}^{vib} = 3nR \frac{x_j^2 e^{x_j}}{(e^{x_j} - 1)^2} - \frac{3nRTa_j}{6} \left[\frac{3x_j^3 e^{3x_j} (x_j - 2) + 12x_j^4 e^{2x_j} + 3x_j^3 e^{x_j} (2 + x_j)}{(e^{x_j} - 1)^4} \right] \quad (6.24a)$$

$$\lim_{x_j \rightarrow \infty} C_{V,qhm,j}^{vib} = 0 \quad (6.24b)$$

$$\lim_{x_j \rightarrow 0} C_{V,qhm,j}^{vib} = 3nR \quad (6.24c)$$

$$\lim_{x_j \rightarrow \infty} C_{V,anh,j}^{vib} = 0 \quad (6.24d)$$

$$\lim_{x_j \rightarrow 0} C_{V,anh,j}^{vib} = -3nRTa_j \quad (6.24e)$$

Thermal pressure

$$P_j^{vib} = \frac{3nRT\gamma_j}{V} \left\{ \frac{x_j}{2} + \frac{x_j}{e^{x_j} - 1} \right\} +$$

$$+ \frac{3nRT^2 a_j \gamma_j}{6V} \left[\frac{1}{2} x_j^2 + \frac{3x_j^2(2-x_j)e^{2x_j} - 3x_j^2(2+x_j)e^{x_j}}{(e^{x_j} - 1)^3} \right] - \frac{3nRT^2 a'_j}{6} \left[\frac{x_j^2}{4} + \frac{3x_j^2 e^{x_j}}{(e^{x_j} - 1)^2} \right] \quad (6.25a)$$

$$\lim_{x_j \rightarrow \infty} P_{qhm,j}^{vib} = \frac{3nRT\gamma_j}{V} \frac{x_j}{2} \quad (6.25b)$$

$$\lim_{x_j \rightarrow 0} P_{qhm,j}^{vib} = \frac{3nRT\gamma_j}{V} \quad (6.25c)$$

$$\lim_{x_j \rightarrow \infty} P_{anh,j}^{vib} = \left(\frac{3nRT^2 a_j \gamma_j}{12V} - \frac{3nRT^2 a'_j}{24} \right) x_j^2 \quad (6.25d)$$

$$\lim_{x_j \rightarrow 0} P_{anh,j}^{vib} = -\frac{3}{2} nRT^2 a'_j \quad (6.25e)$$

Temperature derivative of thermal pressure

$$\left(\frac{\partial P_j^{vib}}{\partial T} \right)_V = \frac{3nR\gamma_j}{V} \frac{x_j^2 e^{x_j}}{(e^{x_j} - 1)^2} + \frac{3nRTa_j \gamma_j}{6V} \left[\frac{3x_j^3 e^{3x_j} (3-x_j) - 12x_j^4 e^{2x_j} - 3x_j^3 e^{x_j} (3+x_j)}{(e^{x_j} - 1)^4} \right] - \frac{3nRTa'_j}{6} \left[\frac{3x_j^3 e^{x_j} (e^{x_j} + 1)}{(e^{x_j} - 1)^3} \right] \quad (6.26a)$$

$$\lim_{x_j \rightarrow \infty} \left(\frac{\partial P_{qhm,j}^{vib}}{\partial T} \right)_V = 0 \quad (6.26b)$$

$$\lim_{x_j \rightarrow 0} \left(\frac{\partial P_{qhm,j}^{vib}}{\partial T} \right)_V = \frac{3nR\gamma_j}{V} \quad (6.26c)$$

$$\lim_{x_j \rightarrow \infty} \left(\frac{\partial P_{anh,j}^{vib}}{\partial T} \right)_V = 0 \quad (6.26d)$$

$$\lim_{x_j \rightarrow 0} \left(\frac{\partial P_{anh,j}^{vib}}{\partial T} \right)_V = -3nRTa'_j \quad (6.26e)$$

Isothermal bulk modulus

$$K_j^{vib} = \frac{3nRT}{V} \left\{ \left(\frac{x_j}{2} + \frac{x_j}{e^{x_j} - 1} \right) \left(\gamma_j^2 + \gamma_j - V \left(\frac{\partial \gamma_j}{\partial V} \right)_T \right) - \frac{\gamma_j^2 x_j^2 e^{x_j}}{(e^{x_j} - 1)^2} \right\} + \frac{3nRT^2 a_j}{6V} \left[\gamma_j - V \left(\frac{\partial \gamma_j}{\partial V} \right)_T \right] \left[\frac{1}{2} x_j^2 + \frac{3x_j^2(2-x_j)e^{2x_j} - 3x_j^2(2+x_j)e^{x_j}}{(e^{x_j} - 1)^3} \right] + \frac{3nRT^2 \gamma_j^2 a_j}{6V} \left[x_j^2 + \frac{e^{3x_j} (12x_j^2 - 15x_j^3 + 3x_j^4) + e^{2x_j} (-24x_j^2 + 12x_j^4) + e^{x_j} (12x_j^2 + 15x_j^3 + 3x_j^4)}{(e^{x_j} - 1)^4} \right] + \frac{3nRT^2 a''_j V}{6} \left[\frac{1}{4} x_j^2 + \frac{3x_j^2 e^{x_j}}{(e^{x_j} - 1)^2} \right] - \frac{3nRT^2 \gamma_j a'_j}{6} \left[\frac{1}{2} x_j^2 + \frac{3x_j^2(2-x_j)e^{2x_j} - 3x_j^2(2+x_j)e^{x_j}}{(e^{x_j} - 1)^3} \right] \quad (6.27a)$$

$$\lim_{x_j \rightarrow \infty} K_{qhm,j}^{vib} = \frac{3nRT}{V} \left\{ \frac{x_j}{2} \left(\gamma_j^2 + \gamma_j - V \left(\frac{\partial \gamma_j}{\partial V} \right)_T \right) \right\} \quad (6.27b)$$

$$\lim_{x_j \rightarrow 0} K_{qhm,j}^{vib} = \frac{3nRT}{V} \left\{ \gamma_j - V \left(\frac{\partial \gamma_j}{\partial V} \right)_T \right\} \quad (6.27c)$$

$$\lim_{x_j \rightarrow \infty} K_{anh,j}^{vib} = \frac{3nRT^2 x_j^2}{V} \left\{ \frac{a_j}{12} \left(\gamma_j - V \left(\frac{\partial \gamma_j}{\partial V} \right)_T \right) + \frac{a_j \gamma_j^2}{6} + \frac{a_j'' V^2}{24} - \frac{\gamma_j a_j' V}{12} \right\} \quad (6.27d)$$

$$\lim_{x_j \rightarrow 0} K_{anh,J}^{vib} = \frac{3}{2} nRT^2 V a_j'' \quad (6.27e)$$

Landau contributions

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This part of the manual contains physical effects which can be represented by the Landau formalism.

The books of Putnis (1992) and Carpenter (1992) form the basis for programming a simple form of the Landau theory in program *'me'*. The thermodynamic properties calculated from the Landau theory are considered as contributions, added to other physical contributions of the Gibbs or Helmholtz energy, such as static, vibrational, electronic, magnetic and defect contributions. We derive the Landau contribution to the Gibbs energy. Three cases are considered; the 2nd order phase transition, the tricritical case and the case of the 1st order phase transition.

7. General equations including all physical effects

The Gibbs energy including all physical effects is written as:

$$G^{total}(P, T) = G(P, T) + G_L(P, T) \quad (7.1)$$

In eqn. (7.1) the term $G(P, T)$ is calculated in '*me*' from the Helmholtz energy, for all contributions except for the Landau contribution. The term $G_L(P, T)$ denotes the Gibbs energy due to the Landau contribution, which is considered as an ordering contribution. From eqn. (7.1) the volume is calculated as:

$$V^{total}(P, T) = V(P, T) + V_L(P, T) \quad (7.2)$$

Thermal expansivity is calculated as:

$$\left(\frac{\partial V^{total}}{\partial T} \right)_P = \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial V_L}{\partial T} \right)_P \quad (7.3)$$

$$\alpha^{total} = \frac{1}{V + V_L} \{ \alpha V + \alpha_L V_L \} \quad (7.4)$$

In eqn. (7.4), α is the thermal expansivity which is calculated in '*me*' as if the Landau contribution were not present.

The bulk modulus is calculated as:

$$\left(\frac{\partial V^{total}}{\partial P} \right)_T = \left(\frac{\partial V}{\partial P} \right)_T + \left(\frac{\partial V_L}{\partial P} \right)_T \quad (7.5)$$

$$K^{total} = \frac{V^{total}}{V/K + V_L/K_L} = \frac{V + V_L}{V/K + V_L/K_L} \quad (7.6)$$

In eqn. (7.6), K is the isothermal bulk modulus calculated in '*me*' as if the Landau contribution were not present.

The other thermodynamic properties such as entropy, enthalpy, heat capacity follow trivially from eqn. (7.1). Once these are known, the isochoric heat capacity is calculated.

The Gibbs energy contribution is written as an expansion of the order parameter Q , which has values between zero and one. Q is defined such that it is zero in the high-temperature phase (HT) and it has values between zero and one in the low-temperature phase (LT). At zero Kelvin the LT phase is stable and the order parameter $Q=1$. At 1 bar the Gibbs energy is given by:

$$G_L = \frac{1}{2} a(T - T_c^0) Q^2 + \frac{1}{4} b^0 Q^4 + \frac{1}{6} c^0 Q^6 + \dots \quad (7.7)$$

We make use of expression (21), p183 of Carpenter (1992) and introduce pressure in eqn. (7.7):

$$G_L = \frac{1}{2} a(T - T_c^0) Q^2 + \frac{1}{4} b^0 Q^4 + \frac{1}{6} c^0 Q^6 + \dots + \frac{1}{2} a_v P Q^2 + \frac{1}{4} b_v P Q^4 + \frac{1}{6} c_v P Q^6 + \dots \quad (7.8)$$

Eqn. (7.8) is rewritten to:

$$G_L = \frac{1}{2}a \left\{ T - \left(T_c^0 - \frac{a_v}{a} P \right) \right\} Q^2 + \frac{1}{4}(b^0 + b_v P) Q^4 + \frac{1}{6}(c^0 + c_v P) Q^6 + \dots \quad (7.9)$$

We recast eqn. (7.9) to:

$$G_L = \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{4}BQ^4 + \frac{1}{6}cQ^6 + \dots \quad (7.10)$$

$$B = b^0 + b_v P$$

$$c = c^0 + c_v P$$

$$T_c = T_c^0 - \frac{a_v}{a} P$$

Eqn. (7.10) illustrates that coefficients B and c are linear functions of pressure and a is a constant. The critical temperature T_c is taken as a linear function of pressure and represents the phase boundary between the HT and LT states. Expressing the critical temperature in the inverse Clapeyron slope, h , we arrive at:

$$T_c = T_c^0 + h \cdot P \quad (7.11)$$

The phase boundary is therefore approximated as a straight line.

8. The 2nd order phase transition ($B>0$ and $c=0$)

For a second order phase transition the contribution to Gibbs energy is given by eqn. (7.10):

$$G_L = \frac{1}{2}a(T-T_c)Q^2 + \frac{1}{4}BQ^4 \quad (8.1)$$

From the equilibrium condition:

$$\frac{dG_L}{dQ} = 0 \quad (8.2)$$

$$Q = \left[\frac{a}{B}(T_c - T) \right]^{1/2} \quad (8.3)$$

By definition $Q=1$ at $T=0$ and therefore:

$$\frac{a}{B} = \frac{1}{T_c} \quad (8.4)$$

As has been shown in eqn. (7.10), a is a constant and B and T_c are linear expressions in pressure. From eqn. (8.4), (7.10) and (7.11) we find that B is composed of the coefficients $b_0=aT_c^0$, and $b_1=ah$.

Substituting eqn. (8.4) into eqn. (8.3) and (8.1) gives:

$$Q = \left(\frac{T_c - T}{T_c} \right)^{1/2} \quad (8.5)$$

$$G_L = \frac{1}{2}a \left\{ (T-T_c)Q^2 + \frac{1}{2}T_cQ^4 \right\} \quad (8.6)$$

We rewrite eqn. (8.5) as:

$$T_c - T = Q^2 T_c \quad (8.7)$$

Inserting eqn. (8.7) into (8.6) gives:

$$G_L = -\frac{1}{4}aQ^4 T_c \quad (8.8)$$

We will make use of the following derivatives by using eqn. (7.11):

$$Q^2 = 1 - T/T_c \quad (8.9a)$$

$$2Q \left(\frac{\partial Q}{\partial T} \right)_P = -\frac{1}{T_c} \quad \text{or} \quad \left(\frac{\partial Q}{\partial T} \right)_P = -\frac{1}{2QT_c} \quad (8.9b)$$

$$2Q \left(\frac{\partial Q}{\partial P} \right)_T = \frac{T}{T_c^2} h \quad \text{or} \quad \left(\frac{\partial Q}{\partial P} \right)_T = \frac{T}{2QT_c^2} h \quad (8.9c)$$

Thermodynamic properties are derived from eqn. (8.8).

a. Entropy

$$S_L = -\left(\frac{\partial G_L}{\partial T}\right)_P = -\frac{1}{2}aQ^2 \quad (8.10)$$

b. Enthalpy

$$H_L = G_L + TS_L = -\frac{1}{4}aQ^4T_c - \frac{1}{2}aTQ^2 \quad (8.11)$$

c. Heat capacity

$$C_{P,L} = T\left(\frac{\partial S_L}{\partial T}\right)_P = \frac{a^2}{2B}T = \frac{aT}{2T_c} = \frac{1}{2}a(1-Q^2) \quad (8.12)$$

d. Volume

$$V_L = \left(\frac{\partial G_L}{\partial P}\right)_T = -\frac{1}{2}ahQ^2\left(1 - \frac{1}{2}Q^2\right) \quad (8.13)$$

e. Isothermal bulk modulus

From eqn. (8.13) we have:

$$\frac{V_L}{K_L} = -\left(\frac{\partial V_L}{\partial P}\right)_T = \frac{1}{2}a\frac{T}{T_c^2}h^2(1-Q^2) \quad (8.14)$$

Note that K_L is infinity at $T=0$, but that $V_L/K_L=0$ at $T=0$ and therefore the last term does not give problems in eqn. (7.6).

f. Thermal expansivity

From eqn. (8.13) we have:

$$\alpha_L V_L = \left(\frac{\partial V_L}{\partial T}\right)_P = \frac{1}{2}ah\frac{1}{T_c}(1-Q^2) \quad (8.15)$$

8.1. Correction for 3rd law

Figure 8.1. shows that a 2nd order phase transition takes place in SiO₂ when it transforms from the stishovite phase to the SiO₂(I) phase having the CaCl₂ structure. Stishovite is the high-temperature phase and does not incorporate a Landau contribution ($Q=0$). Because it is the stable phase at zero temperature and zero pressure, it is unnecessary to correct the entropy for the 3rd law. The situation is different for quartz in which the ordered form is α -quartz, stable at zero temperature and zero pressure. In α -quartz a Landau contribution must be incorporated because it is the low-temperature phase. Quartz is better modelled by the tricritical case discussed in the next section 9. However for the 2nd order case and the tricritical case the corrections in entropy and Gibbs energy are the same. The Landau contribution to entropy at zero Kelvin and zero pressure would be $-0.5a$ at all pressures, violating the 3rd law of entropy. The entropy can be corrected for by adding $+0.5a$ to it. Therefore the Landau contribution at zero Kelvin will be zero at all pressures, just as for the vibrational contribution. The 3rd law correction only affects entropy and Gibbs energy and the correction terms must be added to the expressions for the total Gibbs energy and total entropy:

$$S^{3rdlaw} = +\frac{1}{2}a \quad (8.16)$$

$$G^{3rdlaw} = -\frac{1}{2} aT \quad (8.17)$$

Eqn. (8.17) should be added to eqn. (7.1) to arrive at the complete expression for the Gibbs energy. In program 'me' a switch can be set in the input file to let the 3rd law correction take effect or not.

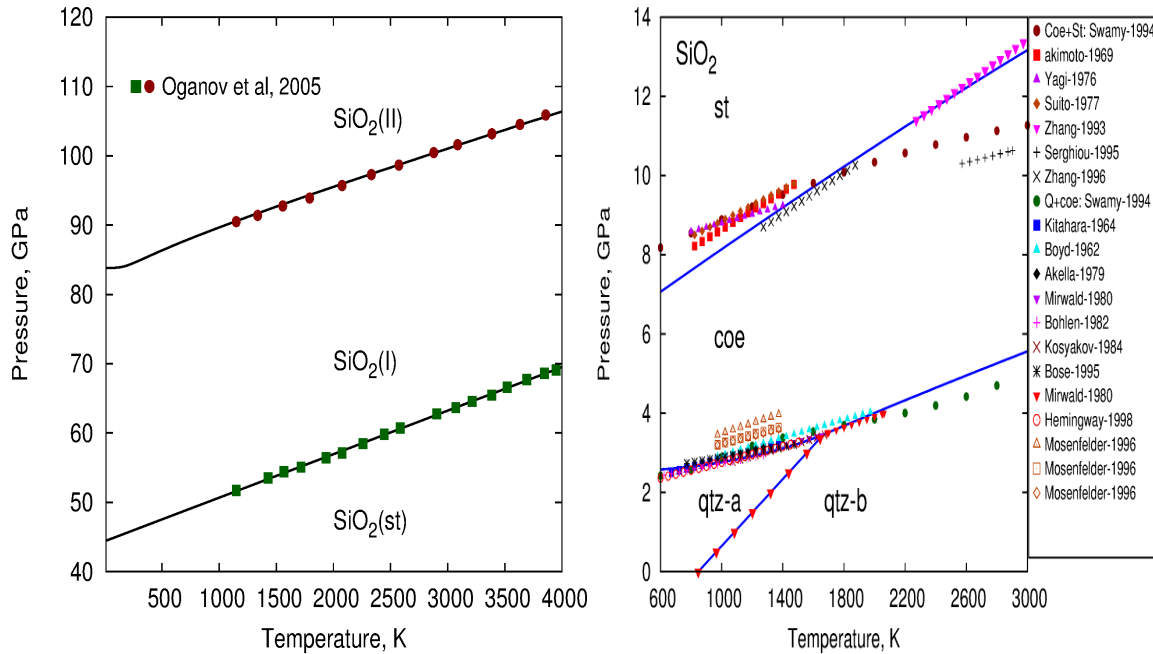


Fig. 8.1. Phase diagrams of SiO₂ determined by Jacobs et al (2019). The left frame illustrates that stishovite (st) is the high-temperature phase stable at 0 K and 0 Pa, and it does not require a correction for the 3rd law. The right frame illustrates that α-quartz (qtz-a) is the low-temperature phase in which ordering takes place. In that phase a correction for the 3rd law is necessary.

8.2. Input file for 'me'

The relevant part of the input file describing the thermodynamic properties of SiO₂ (stishovite) and SiO₂(I) together is given below. The part dealing with the Landau contribution is indicated in blue.

```
<Stishovite>          (* Name of the substance *)
60.084000             (* Mass of the substance in gr/mol *)
3.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-9.09076951448543E+005 (* Static lattice energy in J/mol *)
1.39990948889939E-005 (* Volume/m3/mol at zero K and zero Pa *)
1.38727052441935E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
2                    (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice *)
3                    (* Order of Birch-Murnaghan EoS of the static lattice *)
3.193228000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
4.079847000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero Pa *)
2.312496000000000E+011 (* Static lattice shear modulus/Pa at zero Pa *)
1.805908000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero Pa *)
3.398364000000000E+000 (* Vibrational parameter of the shear modulus *)
1                    (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order*)
1.255646400000000E-002 (* Landau parameter: a *)
6.278232000000000E+006 (* Landau Clapeyron slope Pa/K of the critical phase boundary *)
-7.071347400000000E+003 (* Landau critical temperature at zero pressure Tc0 *)
0.000000000000000E+000 (* Landau 3rd law entropy correction: 0=unnecessary, 1=necessary *)
0                    (* 0=No magnetic contribution, 1=magnetic contribution *)
0                    (* No electronic contribution *)
0                    (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984) *)
0                    (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &...*)
...
```

9. The tricritical phase transition ($B=0$ and $c>0$)

The tricritical phase transition is an intermediate case between 1st order and 2nd order phase transitions. This is the case for example for calcite, CaCO_3 . It gives a symmetry reduction from $R\bar{3}m$ to $R\bar{3}c$ with doubling of the c-axis length, which introduces extra reflections into the diffraction pattern. As calcite is heated the intensity of these extra super lattice reflections decreases as the CO_3 groups disorder and that is a measure for the order parameter Q . Holland and Powell (1998) used the tricritical case also for quartz. The Gibbs energy is given by eqn. (7.10):

$$G_L = \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{6}cQ^6 + \quad (9.1)$$

The equilibrium condition gives

$$\frac{dG_L}{dQ} = 0 \quad (9.2)$$

$$Q^4 = \frac{a}{c}(T_c - T) \quad (9.3)$$

By definition $Q=1$ at $T=0$ and therefore:

$$T_c = \frac{c}{a} \quad (9.4)$$

As has been shown in eqn. (7.10), a is a constant and c and T_c are linear expressions in pressure. From eqn. (9.4), (7.10) and (7.11) we find that c is composed of the coefficients $c_\theta = aT_c^0$, and $c_v = ah$. Substituting eqn. (9.4) into eqn. (9.3) gives:

$$Q^4 = \frac{T_c - T}{T_c} = 1 - T/T_c \quad (9.5)$$

From eqn. (9.1) and (9.4) we have:

$$G_L = \frac{1}{2}a \left\{ (T - T_c)Q^2 + \frac{1}{3}T_c Q^6 \right\} \quad (9.6)$$

Using eqn (9.5) again we have:

$$G_L = -\frac{1}{3}aT_c Q^6 \quad (9.7)$$

In the derivation we make use of temperature and pressure derivatives of the order parameter. By using eqn. (9.5) and (7.11), these derivatives are:

$$4Q^3 \left(\frac{\partial Q}{\partial T} \right)_P = -\frac{1}{T_c} \quad \text{gives} \quad \left(\frac{\partial Q}{\partial T} \right)_P = -\frac{1}{4T_c Q^3} \quad (9.8)$$

$$4Q^3 \left(\frac{\partial Q}{\partial P} \right)_T = \frac{T}{T_c^2} h \quad \text{gives} \quad \left(\frac{\partial Q}{\partial P} \right)_T = \frac{T}{4T_c^2 Q^3} h \quad (9.9)$$

Thermodynamic properties are derived from the Gibbs energy in the same way as for the 2nd order case.

a. Entropy

$$S_L = -\frac{1}{2}aQ^2 \quad (9.10)$$

b. Enthalpy

$$H_L = -\frac{1}{3}aT_cQ^6 - \frac{1}{2}aTQ^2 \quad (9.11)$$

c. Heat capacity

$$C_{P,L} = \frac{aT}{4T_cQ^2} = \frac{aT}{4T_c^{1/2}(T_c - T)^{1/2}} \quad (9.12)$$

d. Volume

Starting from eqn. (9.7) we have:

$$V_L = -\frac{1}{3}ahQ^6 - 2aT_cQ^5 \left(\frac{\partial Q}{\partial P} \right)_T$$

With eqn. (9.9) we have:

$$V_L = -\frac{1}{3}ahQ^6 - \frac{2aT_cQ^2T}{4T_c^2}h = -\frac{1}{3}ahQ^6 - \frac{1}{2}aQ^2h\frac{T}{T_c} = -\frac{1}{2}aQ^2h \left(\frac{2}{3}Q^4 + \frac{T}{T_c} \right)$$

With eqn. (9.5) we have:

$$V_L = -\frac{1}{2}aQ^2h \left(-\frac{1}{3}Q^4 + 1 \right) \quad (9.13)$$

e. Isothermal bulk modulus

From eqn. (9.13) we have:

$$\begin{aligned} \left(\frac{\partial V_L}{\partial P} \right)_T &= -aQ \left(\frac{\partial Q}{\partial P} \right)_T h \left(1 - \frac{1}{3}Q^4 \right) - \frac{1}{2}aQ^2h \left(-\frac{4}{3}Q^3 \left(\frac{\partial Q}{\partial P} \right)_T \right) \\ &= -aQ \frac{T}{4T_c^2Q^3} h^2 \left(1 - \frac{1}{3}Q^4 \right) - \frac{1}{2}aQ^5 \left(-\frac{4}{3} \right) h^2 \frac{T}{4T_c^2Q^3} \\ &= -\frac{aT}{4T_c^2} h^2 \frac{1}{Q^2} \left(1 - \frac{1}{3}Q^4 \right) + \frac{2}{3} \frac{aT}{4T_c^2} h^2 Q^2 \\ &= -\frac{aT}{4T_c^2} h^2 \left\{ \frac{1}{Q^2} \left(1 - \frac{1}{3}Q^4 - \frac{2}{3}Q^4 \right) \right\} \end{aligned}$$

$$\frac{V_L}{K_L} = - \left(\frac{\partial V_L}{\partial P} \right)_T = \frac{aT}{4T_c^2} h^2 \left(\frac{1}{Q^2} - Q^2 \right) \quad (9.14)$$

f. Thermal expansivity

From eqn. (9.13) we have:

$$\begin{aligned}
 \alpha_L V_L &= -aQ \left(\frac{\partial Q}{\partial T} \right)_P h \left(1 - \frac{1}{3} Q^4 \right) - \frac{1}{2} a Q^2 h \left(-\frac{4}{3} Q^3 \left(\frac{\partial Q}{\partial T} \right)_P \right) \\
 &= -aQ \left(-\frac{1}{4T_c Q^3} \right) h \left(1 - \frac{1}{3} Q^4 \right) + \frac{2}{3} a Q^5 h \left(-\frac{1}{4T_c Q^3} \right) \\
 &= \frac{a}{4T_c} h \frac{1}{Q^2} \left(1 - \frac{1}{3} Q^4 \right) - \frac{2}{3} \frac{a}{4T_c} h Q^2 \\
 &= \frac{a}{4T_c} h \left\{ \frac{1}{Q^2} \left(1 - \frac{1}{3} Q^4 \right) - \frac{2}{3} Q^2 \right\} \\
 \alpha_L V_L &= \frac{a}{4T_c} h \left\{ \frac{1}{Q^2} - Q^2 \right\} \tag{9.15}
 \end{aligned}$$

9.1. Correction for 3rd law

Apart from the definition of the order parameter Q , the expression for the Landau contribution to entropy in the tricritical case, eqn. (9.10) is the same as that for the 2nd order case. Therefore the entropy at zero temperature equals $-0.5a$ for all pressures just as for the 2nd order case. The same discussion as in section 8 applies of how the entropy must be corrected for to make the 3rd law of entropy applicable. The corrections that should be added to Gibbs energy and entropy are:

$$S^{3rdlaw} = +\frac{1}{2}a \tag{9.16}$$

$$G^{3rdlaw} = -\frac{1}{2}aT \tag{9.17}$$

Eqn. (9.17) should be added to eqn. (7.1) to arrive at the complete expression for the Gibbs energy. In program 'me' a switch can be set in the input file to let the 3rd law correction take effect or not.

9.2. Input file for 'me'

The relevant part of the input file describing the thermodynamic properties of SiO₂ (α -quartz) and SiO₂ (β -quartz) together is given below. The part dealing with the Landau contribution is indicated in blue.

```

<Quartz-a/b>
60.084000 (* Name of the substance *)
3.0000000000000000E+000 (* Mass of the substance in gr/mol *)
-9.45155560567632E+005 (* Number of atoms in 1 molecular formula unit *)
2.34651170246816E-005 (* Static lattice energy in J/mol *)
2.30353458166755E-005 (* Volume/m3/mol at zero K and zero Pa *)
2 (* Volume/m3/mol of the static lattice at zero Pa *)
3 (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice *)
4.2623220000000000E+010 (* Order of Birch-Murnaghan EoS of the static lattice *)
5.3692230000000000E+000 (* Static lattice bulk modulus/Pa at zero Pa *)
4.9734650000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero Pa *)
1.1000000000000000E+000 (* Static lattice shear modulus/Pa at zero Pa *)
2.4000000000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero Pa *)
2 (* Vibrational parameter of the shear modulus *)
1.1461375280000000E+001 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
4.2258592500000000E+006 (* Landau parameter: a *)
8.4700000000000000E+002 (* Landau Clapeyron slope Pa/K of the critical phase boundary *)
8.4700000000000000E+002 (* Landau critical temperature at zero pressure Tc0 *)

```



```
1.0000000000000000E+000 (* Landau 3rd law entropy correction: 0=unnecessary, 1=necessary *)
0 (* 0=No magnetic contribution, 1=magnetic contribution *)
0 (* No electronic contribution *)
0 (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984) *)
0 (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &...*)
.
.
```

10. First order transition ($B < 0$, $a > 0$, $c > 0$)

The Gibbs energy expression is given by eqn. (7.10):

$$G_L = \frac{1}{2}a(T-T_c)Q^2 + \frac{1}{4}BQ^4 + \frac{1}{6}cQ^6 + \dots \quad (10.1)$$

Applying the equilibrium condition gives:

$$\frac{dG_L}{dQ} = 0 \quad (10.2)$$

$$Q^2 = \frac{-B \pm [B^2 - 4ac(T-T_c)]^{1/2}}{2c} \quad (10.3)$$

In Figure 8.23 of Putnis' (1992) book, Gibbs energies are plotted as function of the order parameter. The transition temperature, T_R , is characterized by the minimum in the Gibbs energy curve and its zero point where $Q=Q_0$. The Gibbs energy starts at $Q=0$ having the value zero, goes through a maximum when Q increases, and subsequently passes a minimum which is located at $G_L=0$. The transition temperature is given by two equations as:

$$\frac{dG_L}{dQ} = 0: \quad Q \{ a(T_R - T_c) + BQ^2 + cQ^4 \} = 0 \quad (10.4)$$

$$2^{\text{nd}} \text{ zero point:} \quad Q^2 \left\{ \frac{1}{2}a(T_R - T_c) + \frac{1}{4}BQ^2 + \frac{1}{6}cQ^4 \right\} = 0 \quad (10.5)$$

Eqn (10.4) and (10.5) give:

$$a(T_R - T_c) + BQ^2 + cQ^4 = 0$$

$$a(T_R - T_c) + \frac{1}{2}BQ^2 + \frac{1}{3}cQ^4 = 0$$

Eliminating the first term by subtraction gives:

$$Q_0^2 = -\frac{3}{4} \frac{B}{c} \quad (10.6)$$

Substituting eqn. (10.6) into the first equation gives:

$$T_R = T_c + \frac{3B^2}{16ac} \quad (10.7)$$

Eqn. (10.7) indicates that the transition temperature is larger than the critical temperature. We express thermodynamic properties in terms of the transition temperature T_R . From eqn. (10.6) and (10.7) it follows that:

$$Q_0 = \left\{ \frac{-4a(T_R - T_c)}{B} \right\}^{1/2} \quad (10.8)$$

Parameter Q_0 is the order parameter when the temperature equals T_R . Substituting eqn. (10.7) into the expression for the Gibbs energy, eqn. (10.1) becomes:

$$G_L = \frac{1}{2}a \left(T - T_R + \frac{3B^2}{16ac} \right) Q^2 + \frac{1}{4}BQ^4 + \frac{1}{6}cQ^6 \quad (10.9)$$

The Gibbs energy may be expressed in Q_0 by substituting B with eqn. (10.6):

$$G_L = \frac{1}{2}a \left(T - T_R + \frac{Q_0^4 c}{3a} \right) Q^2 - \frac{1}{3}Q_0^2 c Q^4 + \frac{1}{6}cQ^6 \quad (10.10)$$

Using eqn. (10.3) the order parameter is expressed in T_R :

$$Q^2 = \frac{-B \pm \left[\frac{1}{4}B^2 + 4ac(T_R - T) \right]^{1/2}}{2c} \quad (10.11)$$

The order parameter is expressed in the order parameter Q_0 by combining eqn (10.11) and (10.6) and the fact that $Q=Q_0$ at $T=T_R$:

$$Q^2 = \frac{2}{3}Q_0^2 + \left[\frac{1}{9}Q_0^4 + \frac{a}{c}(T_R - T) \right]^{1/2} \quad (10.12)$$

The phase boundary between the two phases is expressed in the inverse Clapeyron slope, h , and it is assumed to be a straight line:

$$T_R = T_R^0 + hP \quad (10.13)$$

a. Entropy

Entropy is derived from eqn. (10.10) as:

$$\begin{aligned} -S_L &= \left(\frac{\partial G_L}{\partial T} \right)_P \\ -S_L &= \frac{1}{2}aQ^2 + \left\{ a \left(T - T_R + \frac{Q_0^4 c}{3a} \right) - \frac{4}{3}Q_0^2 c Q^2 + cQ^4 \right\} Q \left(\frac{\partial Q}{\partial T} \right)_P \end{aligned}$$

The second term on the right-hand side of this equation equals zero, which can be found by substituting eqn. (10.11):

$$\begin{aligned} a \left(T - T_R + \frac{Q_0^4 c}{3a} \right) - \frac{4}{3}Q_0^2 c Q^2 + cQ^4 &= a(T - T_R) + \frac{1}{3}Q_0^4 c - \frac{4}{3}Q_0^2 c \left\{ \frac{2}{3}Q_0^2 + \left[\frac{1}{9}Q_0^4 + \frac{a}{c}(T_R - T) \right]^{1/2} \right\} + \\ &= c \left\{ \frac{2}{3}Q_0^2 + \left[\frac{1}{9}Q_0^4 + \frac{a}{c}(T_R - T) \right]^{1/2} \right\}^2 = 0 \end{aligned} \quad (10.14)$$

The entropy becomes: $S_L = -\frac{1}{2}aQ^2$ (10.15)

b. Volume

Volume contribution is derived from eqn. (10.10) by differentiation to pressure. In that case also the order parameter given by (10.12) must be differentiated to pressure. From the condition that $Q=1$ at zero Kelvin, it appears that one of the parameters in (10.12) is a function of pressure by virtue of eqn. (10.13). The condition gives:

$$\left(1 - \frac{2}{3}Q_0^2\right)^2 - \frac{1}{9}Q_0^4 = \frac{a}{c}T_R$$
 (10.16)

We select ‘ c ’ to be pressure dependent, and treat ‘ a ’ and Q_0 as constants. In that case:

$$c = \frac{aT_R}{\left(1 - \frac{2}{3}Q_0^2\right)^2 - \frac{1}{9}Q_0^4}, \text{ and } \left(\frac{\partial c}{\partial P}\right)_T = \frac{ah}{\left(1 - \frac{2}{3}Q_0^2\right)^2 - \frac{1}{9}Q_0^4}$$
 (10.17)

Differentiating the Gibbs energy contribution, eqn. (10.10) to pressure gives:

$$V_L = \left\{ a \left(T - T_R + \frac{Q_0^4 c}{3a} \right) - \frac{4}{3}Q_0^2 c Q^2 + c Q^4 \right\} Q \left(\frac{\partial Q}{\partial P} \right)_T + \frac{1}{2} a \left(-h + \frac{Q_0^4}{3a} \left(\frac{\partial c}{\partial P} \right)_T \right) Q^2 - \frac{1}{3} Q_0^2 \left(\frac{\partial c}{\partial P} \right)_T Q^4 + \frac{1}{6} \left(\frac{\partial c}{\partial P} \right)_T Q^6$$
 (10.18)

The first term on the right-hand side equals zero, by virtue of eqn. (10.14), and the volume contributions becomes:

$$V_L = \frac{1}{2} a \left(-h + \frac{Q_0^4}{3a} \left(\frac{\partial c}{\partial P} \right)_T \right) Q^2 - \frac{1}{3} Q_0^2 \left(\frac{\partial c}{\partial P} \right)_T Q^4 + \frac{1}{6} \left(\frac{\partial c}{\partial P} \right)_T Q^6$$
 (10.19)

By substitution $Q_0=0$, we obtain the expression for the tricritical case, eqn. (9.13).

c. Heat capacity

Heat capacity is expressed as:

$$C_{P,L} = T \left(\frac{\partial S_L}{\partial T} \right)_P = -aT Q \left(\frac{\partial Q}{\partial T} \right)_P$$
 (10.20)

In this case we must differentiate the order parameter, eqn. (10.12) to temperature. We use the expression for c in eqn. (10.17) to find that $\left(\frac{\partial c}{\partial T}\right)_P = 0$:

$$2Q \left(\frac{\partial Q}{\partial T} \right)_P = \frac{1}{2} \left[\frac{1}{9}Q_0^4 + \frac{a}{c}(T_R - T) \right]^{-1/2} \left(-\frac{a}{c} \right)$$

$$\left(\frac{\partial Q}{\partial T} \right)_P = -\frac{a}{4cQ} \left[\frac{1}{9}Q_0^4 + \frac{a}{c}(T_R - T) \right]^{-1/2}$$

Heat capacity becomes:

$$C_{P,L} = \frac{a^2 T}{4c} \left[\frac{1}{9} Q_0^4 + \frac{a}{c} (T_R - T) \right]^{-1/2} \quad (10.21)$$

When $Q_0=0$, we obtain the expression for the tricritical case, eqn. (9.12). That is found by substituting $Q_0=0$ in the expression for the order parameter, eqn. (10.12) and in the expression for c in eqn. (10.17).

d. Thermal expansivity

To obtain $\alpha_L V_L$ in expression (7.4) we use the Maxwell relation:

$$\left(\frac{\partial S_L}{\partial P} \right)_T = - \left(\frac{\partial V_L}{\partial T} \right)_P = -\alpha_L V_L \quad (10.22)$$

$$\alpha_L V_L = aQ \left(\frac{\partial Q}{\partial P} \right)_T \quad (10.23)$$

In that case we need the pressure derivative of the order parameter, eqn. (10.12):

$$2Q \left(\frac{\partial Q}{\partial P} \right)_T = \frac{1}{2} \left[\frac{1}{9} Q_0^4 + \frac{a}{c} (T_R - T) \right]^{-1/2} \left\{ \frac{ah}{c} + (T_R - T) \left(-\frac{a}{c^2} \right) \left(\frac{\partial c}{\partial P} \right)_T \right\}$$

$$\left(\frac{\partial Q}{\partial P} \right)_T = \frac{a}{4Qc^2} \left[\frac{1}{9} Q_0^4 + \frac{a}{c} (T_R - T) \right]^{-1/2} \left(hc - (T_R - T) \left(\frac{\partial c}{\partial P} \right)_T \right) \quad (10.24)$$

Using expression (10.17):

$$\left(\frac{\partial c}{\partial P} \right)_T = \frac{ah}{\left(1 - \frac{2}{3} Q_0^2 \right)^2 - \frac{1}{9} Q_0^4} \quad (10.25)$$

$$\alpha_L V_L = \frac{a^2}{4c^2} \left[\frac{1}{9} Q_0^4 + \frac{a}{c} (T_R - T) \right]^{-1/2} \left(hc - (T_R - T) \left(\frac{\partial c}{\partial P} \right)_T \right) \quad (10.26)$$

In *tricritical* case, $Q_0=0$, we have:

$$\alpha_L V_L = \frac{a^2}{4c^2} \left[\frac{a}{c} (T_R - T) \right]^{-1/2} (hc - ah(T_R - T))$$

With (10.17), $c=aT_R$, and $Q^4=(a/c)(T_R-T)$ we have:

$$\alpha_L V_L = \frac{ahT}{4T_R^2 Q^2} = \frac{ah}{4T_R Q^2} \frac{T}{T_R} = \frac{ah}{4T_R Q^2} (1 - Q^4) = \frac{ah}{4T_R} \left(\frac{1}{Q^2} - Q^2 \right), \text{ which is eqn. (9.15)}$$

e. Bulk modulus

To obtain V_L/K_L in expression (7.4) we use eqn. (10.19) for volume:

$$\frac{V_L}{K_L} = -\left(\frac{\partial V_L}{\partial P}\right)_T \quad (10.27)$$

$$V_L = \frac{1}{2}a\left(-h + \frac{Q_0^4}{3a}\left(\frac{\partial c}{\partial P}\right)_T\right)Q^2 - \frac{1}{3}Q_0^2\left(\frac{\partial c}{\partial P}\right)_T Q^4 + \frac{1}{6}\left(\frac{\partial c}{\partial P}\right)_T Q^6 \quad (10.19)$$

Because the pressure derivative $(\partial c/\partial P)_T$ does not depend on pressure:

$$\frac{V_L}{K_L} = -\left\{a\left(-h + \frac{Q_0^4}{3a}\left(\frac{\partial c}{\partial P}\right)_T\right) - \frac{4}{3}Q_0^2\left(\frac{\partial c}{\partial P}\right)_T Q^2 + \left(\frac{\partial c}{\partial P}\right)_T Q^4\right\}Q\left(\frac{\partial Q}{\partial P}\right)_T \quad (10.28)$$

The pressure derivative of Q is given by eqn. (10.24). The pressure derivative of c is given by (10.25).

In the tricritical case $Q_0=0$. Using eqn. (10.17) for $c=aT_R$, eqn. (10.12) for $Q^4=(a/c)(T_R-T)$, and eqn. (10.25) for $(\partial c/\partial P)_T=ah$, it follows eqn. (9.14).

10.1. Entropy and volume differences along the phase boundary; determine a , B and c

We fix the Clapeyron slope for the phase transition. The phase transition is prescribed by a straight line, given by eqn. (10.13).

$$T_R = T_R^0 + hP = T_R^0 + \frac{\Delta V}{\Delta S}P \quad (10.29)$$

In eqn. (10.29), ΔV , and ΔS are volume and entropy difference between the high and low temperature phase at the phase boundary with temperature T_R .

$$\Delta V = V^{HT} - V^{LT} = V^{HT} - (V^{HT} + V_L) = -V_L \quad (10.30a)$$

$$\Delta S = S^{HT} - S^{LT} = S^{HT} - (S^{HT} + S_L) = -S_L \quad (10.30b)$$

Using eqn. (10.15) and (10.19) and setting $T=T_R$:

$$\Delta S = \frac{1}{2}aQ_0^2 \quad (10.31)$$

$$-\Delta V = \frac{1}{2}a\left(-h + \frac{Q_0^4}{3a}\left(\frac{\partial c}{\partial P}\right)_T\right)Q_0^2 - \frac{1}{3}Q_0^2\left(\frac{\partial c}{\partial P}\right)_T Q_0^4 + \frac{1}{6}\left(\frac{\partial c}{\partial P}\right)_T Q_0^6 = -\frac{1}{2}ahQ_0^2$$

$$\Delta V = \frac{1}{2}ahQ_0^2 \quad (10.32)$$

The transition enthalpy is:

$$\Delta H = T_R\Delta S = \frac{1}{2}aT_RQ_0^2 \quad (10.33)$$

The coefficients are determined as follows. We select the inverse Clapeyron slope, h , and temperature T_R^0 on the phase boundary at 1 bar, by using experimental values. We take the experimental value for ΔH at 1 bar at the transition. Because the phase boundary is assumed to be a straight line, it does not depend on temperature and pressure. Next we select a value for Q_0 , e.g. 0.7.

Eqn. (10.33) gives than the value for a . The value for ‘ c ’ is than calculated by eqn. (10.17). The value of B is calculated by eqn. (10.6).

10.2. Example: Quartz (α, β)

Hemingway (1994) established a transition enthalpy of 627.63 J/mol at 1 bar and 847 K. The transition entropy is than 0.741 J/K/mol. The phase boundary between α and β quartz is given by:

$$T_R = 847 + 236.63826P / GPa$$

Because $h = \Delta V / \Delta S = 2.3663826 \times 10^{-7} \text{ Pa}^{-1}$, the volume difference is: $\Delta V = 1.7535 \times 10^{-7} \text{ m}^3/\text{mol}$

We estimate the value of $Q_0 = 0.7$. Q_0 is taken constant. At $P=0$ we have:

$$\text{Eqn. (10.33): } \Delta H = T_R \Delta S = \frac{1}{2} a T_R Q_0^2 \quad a = 3.0245$$

$$\text{Eqn. (10.17): } c = \frac{a T_R}{\left(1 - \frac{2}{3} Q_0^2\right)^2 - \frac{1}{9} Q_0^4} \quad c = 6003.6360$$

$$\text{Eqn. (10.6): } Q_0^2 = -\frac{3}{4} \frac{B}{c} \quad B = -3922.3755$$

$$\text{Eqn. (10.7): } T_R = T_c + \frac{3B^2}{16ac} \quad T_R^0 = T_c^0 + 158.8662$$

$$\text{Eqn (10.15): } S_L(T=0) = -1.5166 \text{ J / K / mol}$$

10.3. Entropy at 0 K and the 3rd law of thermodynamics

At zero Kelvin, the entropy is obtained from eqn. (10.25) as:

$$S_L(T=0) = -\frac{1}{2} a \quad (10.34)$$

The entropy is therefore negative, just as found in section (10.2), violating the 3rd law of thermodynamics.

Here we correct the entropy for the 3rd law correction. The total entropy of the HT or LT form is described with a single equation derived from eqn. (7.1).

$$S^{total} = S + S_L + S_{cor}$$

For the entropy correction we subtract the Landau contribution at 0 K:

$$S^{total} = S + S_L - S_L(T=0) = S + S_L + \frac{1}{2} a \quad (10.35)$$

Equation (7.1) for the Gibbs energy is than corrected as:

$$G^{total} = G + G_L + \frac{1}{2} a T \quad (10.36)$$

10.4. Input file for 'me'

The relevant part of the input file describing the thermodynamic properties of SiO₂ (α -quartz) and SiO₂ (β -quartz) together is given below. The part dealing with the Landau contribution is indicated in blue.

```
<Quartz-a/b> (* Name of the substance *)
 60.084000 (* Mass of the substance in gr/mol *)
 3.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-9.45129758567632E+005 (* Static lattice energy in J/mol *)
 2.34675261797908E-005 (* Volume/m3/mol at zero K and zero Pa *)
 2.30557293464477E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
 2 (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice *)
 3 (* Order of Birch-Murnaghan EoS of the static lattice *)
 4.287372000000000E+010 (* Static lattice bulk modulus/Pa at zero Pa *)
 5.285657000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero Pa
0.000000000000000E+000 (* Static lattice shear modulus/Pa at zero Pa *)
0.000000000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero Pa
0.000000000000000E+000 (* Vibrational parameter of the shear modulus *)
 3 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order
6.272700000000000E+002 (* Landau parameter: transition enthalpy/J/mol at 1 bar *)
4.225859250000000E+006 (* Landau Clapeyron slope Pa/K of the critical phase boundary *)
8.470000000000000E+002 (* Landau critical temperature at zero pressure  $T_c^0$  *)
 7.000000000000000E-001 (* Order parameter at the transition  $Q_0$  *)
 1.000000000000000E+000 (* Landau 3rd law entropy correction: 0=unnecessary, 1=necessary *)
 0 (* 0=No magnetic contribution, 1=magnetic contribution *)
 0 (* No electronic contribution *)
 0 (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984) *)
 0 (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &...*)
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Magnetic contributions

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This part of the manual contains a description for the magnetic contribution derived from Inden's (1981) formalism.

Some basic approximate formulations of Inden's (1981) formalism are given by Hillert and Jarl (1981).

The thermodynamic properties calculated from Inden's (1981) formalism are considered as contributions, added to other physical contributions of the Gibbs or Helmholtz energy, such as static, vibrational, and electronic contributions.

11 Inden's (1981) method for magnetic lambda transitions

Inden's (1981) method is an empirical theory for the description of magnetic lambda transitions, originally developed for metals. The theory formulates expressions for the isobaric heat capacity from which the Gibbs energy is derived. Because Inden's model results in complicated expressions for the Gibbs energy, Hillert and Jarl (1979) have simplified them by developing the heat capacity in MacLaurin series in which only three terms are taken into account. These approximate expressions for thermodynamic properties are widely used in the Calphad community. The disadvantage of using only three terms in the series expansion is that the results deviate from Inden's original model, especially near the critical point. The series in the formalism are constants which can be calculated beforehand. In **XiPT** these constants are calculated for each end member in each phase at reading-in the input data file. We follow that approach in '*me*' too. Therefore treating many terms in the series expansion is computationally just as cheap as using only 3 terms; there is no reason to truncate the series expansion after just three terms. The full series expansion is not given in the literature. It is given below.

We have modified Inden's original formalism by writing the same expressions not for the isobaric heat capacity, but for the isochoric heat capacity. The advantage is that an expression for the Helmholtz energy can be derived, which serves as a contribution to the total expression for the Helmholtz energy composed of static, vibrational, and electronic contributions, such as demonstrated by Jacobs and de Jong (2009). Additionally the formalism is reconstructed in such way that the magnetic contribution to entropy is zero at zero temperature, see Jacobs and de Jong (2009). Contrasted to Calphad the 3rd law of thermodynamics is obeyed in the formalism presented here.

11.1. Derivation of thermodynamic properties

The heat capacity is written as:

$$C_V^\lambda = a_1 \ln\left(\frac{1+\tau^m}{1-\tau^m}\right) n_a R \ln(1+\beta) \quad \tau \leq 1 \quad (11.1)$$

$$C_V^\lambda = a_2 \ln\left(\frac{\tau^n+1}{\tau^n-1}\right) n_a R \ln(1+\beta) \quad \tau > 1 \quad (11.2)$$

In Eqn's (11.1) and (11.2) τ represents T/T_c with T_c the critical temperature and β the average magnetic moment expressed in Bohr-magneton. In Inden's formalism the magnetic moment is assumed temperature independent. Values for m and n are larger than 1. For the benefit of integration to temperature, these expressions are developed in MacLaurin series by Hillert and Jarl (1979), which we recast as:

$$C_V^\lambda(\tau \leq 1) = 2a_1 n_a R \sum_{j=0}^{\infty} \frac{\tau^{(2j+1)m}}{2j+1} \ln(1+\beta) \quad (11.3)$$

$$C_V^\lambda(\tau > 1) = 2a_2 n_a R \sum_{j=0}^{\infty} \frac{\tau^{-(2j+1)n}}{2j+1} \ln(1+\beta) \quad (11.4)$$

Convergence of the series to within 0.1% in heat capacity is achieved after about 20 terms for Nickel. After integration to temperature at constant volume one finds the Helmholtz energy and entropy below:

$$A^\lambda = n_a \cdot g(\tau) \cdot RT \ln(1 + \beta) \quad (11.5)$$

$$g(\tau \leq 1) = -\frac{2a_1}{m} \sum_{j=0}^{\infty} \frac{\tau^{(2j+1)m} - \tau^{-1}}{(2j+1)^2 [(2j+1)m+1]} - \tau^{-1} + \frac{2a_2}{n} \sum_{j=0}^{\infty} \frac{\tau^{-1}}{(2j+1)^2 [-(2j+1)n+1]} \quad (11.6)$$

$$g(\tau > 1) = -1 + \frac{2a_2}{n} \sum_{j=0}^{\infty} \frac{\tau^{-(2j+1)n}}{(2j+1)^2 [-(2j+1)n+1]} \quad (11.7)$$

$$S^\lambda = -\left(\frac{\partial A^\lambda}{\partial T}\right)_V = -n_a \cdot R \left\{ g(\tau) + \tau \left(\frac{\partial g}{\partial \tau}\right)_V \right\} \ln(1 + \beta) \quad (11.8)$$

$$C_V^\lambda = T \left(\frac{\partial S^\lambda}{\partial T}\right)_V = -n_a \cdot R \tau \left\{ 2 \left(\frac{\partial g}{\partial \tau}\right)_V + \tau \left(\frac{\partial^2 g}{\partial \tau^2}\right)_V \right\} \ln(1 + \beta) \quad (11.9)$$

The entropy is zero at zero Kelvin, commensurate with the 3rd law of thermodynamics. At infinite temperatures it is $+n_a R \ln(1 + \beta)$ in accordance with quantum mechanics, see e.g. Wu et al. (2009). Constant n_a represents the number of atoms giving rise to magnetic contribution in a molecular formula unit, for instance, in Fe_2SiO_4 (fayalite) this number would be 2. The simplified expression for entropy used in the Calphad community, has the negative value of $-n_a R \ln(1 + \beta)$ at zero temperature, and zero at infinite temperature. The energy in our formalism is defined zero at infinite temperature leading to a magnetic contribution to energy at zero temperature and zero pressure relative to the lattice without magnetic interactions.

The coefficients a_1 and a_2 are written as (see section 11.4):

$$a_1 = m \left[1 - \frac{m}{\frac{s_2}{s_1} \left(1 - \frac{1}{p}\right) n + m} \right] \frac{1}{2 \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2}} \quad (11.10)$$

$$a_2 = \left[\frac{m}{\frac{s_2}{s_1} \left(1 - \frac{1}{p}\right) + \frac{m}{n}} \right] \frac{1}{2 \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2}} \quad (11.11)$$

$$s_1 = \sum_{j=0}^{\infty} \frac{1}{(2j+1)[(2j+1)m+1]} \quad (11.12)$$

$$s_2 = \sum_{j=0}^{\infty} \frac{1}{(2j+1)[-(2j+1)n+1]} \quad (11.13)$$

The magnetic contribution to thermodynamic properties is therefore described in terms of m , n and p . The coefficient p denotes the ratio of the magnetic energy above the Curie temperature and the total magnetic energy. In formula:

$$p = \frac{\int_0^{\infty} C_V^\lambda d\tau}{\int_0^{\infty} C_V^\lambda d\tau} \quad (11.14)$$

Some useful derivatives are:

$$\left(\frac{\partial g}{\partial \tau}\right)_T (\tau \leq 1) = \left\{ -2a_1 \sum_{j=0}^{\infty} \frac{\tau^{(2j+1)m-1}}{(2j+1)[(2j+1)m+1]} - \frac{2a_1}{m} \sum_{j=0}^{\infty} \frac{\tau^{-2}}{(2j+1)^2[(2j+1)m+1]} + \tau^{-2} + \right. \\ \left. - \frac{2a_2}{n} \sum_{j=0}^{\infty} \frac{\tau^{-2}}{(2j+1)^2[-(2j+1)n+1]} \right\} \quad (11.15)$$

$$\left(\frac{\partial g}{\partial \tau}\right)_T (\tau > 1) = -2a_2 \sum_{j=0}^{\infty} \frac{\tau^{-(2j+1)n-1}}{(2j+1)[-(2j+1)n+1]} \quad (11.16)$$

$$\left(\frac{\partial^2 g}{\partial \tau^2}\right)_T (\tau \leq 1) = -2a_1 \sum_{j=0}^{\infty} \frac{\tau^{(2j+1)m-2}[(2j+1)m-1]}{(2j+1)[(2j+1)m+1]} + \frac{4a_1}{m} \sum_{j=0}^{\infty} \frac{\tau^{-3}}{(2j+1)^2[(2j+1)m+1]} - 2\tau^{-3} + \\ + \frac{4a_2}{n} \sum_{j=0}^{\infty} \frac{\tau^{-3}}{(2j+1)^2[-(2j+1)n+1]} \quad (11.17)$$

$$\left(\frac{\partial^2 g}{\partial \tau^2}\right)_T (\tau > 1) = -2a_2 \sum_{j=0}^{\infty} \frac{\tau^{-(2j+1)n-2}[-(2j+1)n-1]}{(2j+1)[-(2j+1)n+1]} \quad (11.18)$$

$$Z_C \equiv 2 \left(\frac{\partial g}{\partial \tau}\right)_T + \tau \left(\frac{\partial^2 g}{\partial \tau^2}\right)_T (\tau \leq 1) = -2a_1 \sum_{j=0}^{\infty} \frac{\tau^{(2j+1)m-1}}{2j+1} \quad (11.19)$$

$$Z_C \equiv 2 \left(\frac{\partial g}{\partial \tau}\right)_T + \tau \left(\frac{\partial^2 g}{\partial \tau^2}\right)_T (\tau > 1) = -2a_2 \sum_{j=0}^{\infty} \frac{\tau^{-(2j+1)n-1}}{2j+1} \quad (11.20)$$

$$Z_S \equiv g(\tau) + \tau \left(\frac{\partial g}{\partial \tau}\right)_T (\tau \leq 1) = -\frac{2a_1}{m} \sum_{j=0}^{\infty} \frac{\tau^{(2j+1)m}}{(2j+1)^2} \quad (11.21)$$

$$Z_S \equiv g(\tau) + \tau \left(\frac{\partial g}{\partial \tau}\right)_T (\tau > 1) = -1 + \frac{2a_2}{n} \sum_{j=0}^{\infty} \frac{\tau^{-(2j+1)n}}{(2j+1)^2} \quad (11.22)$$

Because in this formalism the magnetic properties are only temperature dependent, the Gibbs energy contribution equals that of the Helmholtz energy contribution. The enthalpy contribution equals the energy contribution. The magnetic contribution to isobaric heat capacity and isochoric heat capacity are equal. The formalism does not change the total volume, thermal expansivity and bulk modulus.

11.2. Limiting values for magnetic contributions to thermodynamic properties

Helmholtz energy at $T=0$

The Helmholtz energy at $T = 0$ is derived from eqn. (11.5) and (11.6):

$$A^\lambda = n_a \cdot g(\tau) \cdot RT \ln(1 + \beta) \quad (11.5)$$

$$g(\tau \leq 1) = -\frac{2a_1}{m} \sum_{j=0}^{\infty} \frac{\tau^{(2j+1)m} - \tau^{-1}}{(2j+1)^2 [(2j+1)m+1]} - \tau^{-1} + \frac{2a_2}{n} \sum_{j=0}^{\infty} \frac{\tau^{-1}}{(2j+1)^2 [-(2j+1)n+1]} \quad (11.6)$$

Rewrite (11.5) to:

$$A^\lambda = n_a \cdot g(\tau) \cdot \tau \cdot RT_c \cdot \ln(1 + \beta)$$

$$A^\lambda(\tau = 0) = \left\{ \frac{2a_1}{m} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2 [(2j+1)m+1]} - 1 + \frac{2a_2}{n} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2 [-(2j+1)n+1]} \right\} RT_c \ln(1 + \beta) \quad (11.23)$$

Entropy at $T=0$

Combining eqn. (11.8) and (11.21) gives:

$$S^\lambda(\tau = 0) = 0 \quad (11.24)$$

Energy at $T=0$

Combining eqn. (11.23) and (11.24):

$$U^\lambda(\tau = 0) = A^\lambda(T = 0) \quad (11.25)$$

Isochoric heat capacity at $T=0$

Combining eqn. (11.9) and (11.19):

$$C_V^\lambda(\tau = 0) = 0 \quad (11.26)$$

Eqn. (11.26) holds when $m > 1$, which is normally the case.

Helmholtz energy expression at $T \rightarrow \infty$

The Helmholtz energy at $T = 0$ is derived from eqn. (11.5) and (11.7):

$$A^\lambda = n_a \cdot g(\tau) \cdot RT \ln(1 + \beta) \quad (11.5)$$

$$g(\tau > 1) = -1 + \frac{2a_2}{n} \sum_{j=0}^{\infty} \frac{\tau^{-(2j+1)n}}{(2j+1)^2 [-(2j+1)n+1]} \quad (11.7)$$

$$\lim_{\tau \rightarrow \infty} A^\lambda = -n_a RT \ln(1 + \beta) \quad (11.27)$$

Entropy expression at $T \rightarrow \infty$

Combining eqn. (11.8) and (11.22):

$$\lim_{\tau \rightarrow \infty} S^\lambda = n_a R \ln(1 + \beta) \quad (11.28)$$

Isochoric heat capacity expression at $T \rightarrow \infty$

Combining eqn. (11.9) and (11.20):

$$C_V^\lambda(\tau = 0) = 0 \tag{11.29}$$

11.3. Three terms in the MacLaurin series: Calphad formalism and repairing it for 3rd law

We derive the Helmholtz energy starting from eqn. (11.5). In the Calphad formalism, $m=3$ and $n=5$ and just 3 terms in the series expansion are taken into account.

4. For temperatures below the critical temperature we have with eqn. (11.6):

Taking 3 terms in (11.6) gives:

$$g(\tau \leq 1) = -\frac{2a_1}{m} \left\{ \frac{\tau^m - \tau^{-1}}{m+1} + \frac{\tau^{3m} - \tau^{-1}}{9(3m+1)} + \frac{\tau^{5m} - \tau^{-1}}{25(5m+1)} \right\} - \tau^{-1} + \frac{2a_2}{n} \left\{ \frac{\tau^{-1}}{-n+1} + \frac{\tau^{-1}}{9(-3n+1)} + \frac{\tau^{-1}}{25(-5n+1)} \right\}$$

Inserting values $m=3$ and $n=5$ gives:

$$\begin{aligned} g(\tau \leq 1) &= -\frac{2a_1}{3} \left\{ \frac{\tau^3}{4} + \frac{\tau^9}{90} + \frac{\tau^{15}}{400} - \frac{37960 \tau^{-1}}{144000} \right\} - \tau^{-1} - \frac{2a_2}{5} \left\{ \frac{1}{4} + \frac{1}{126} + \frac{1}{600} \right\} \tau^{-1} \\ g(\tau \leq 1) &= -a_1 \left\{ \frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} - \frac{949 \tau^{-1}}{5400} \right\} - \tau^{-1} - a_2 \frac{3271}{31500} \tau^{-1} \\ g(\tau \leq 1) &= -a_1 \left\{ \frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right\} + \tau^{-1} \left\{ \frac{949}{5400} a_1 - 1 - \frac{3271}{31500} a_2 \right\} \end{aligned} \quad (11.30)$$

From eqn. (11.12) and (11.13) we have:

$$\begin{aligned} s_1 &= \frac{71}{240} \\ s_2 &= -\frac{711}{2520} \\ \frac{s_2}{s_1} &= -\frac{474}{497} \\ \frac{1}{2 \sum_{j=0}^2 \frac{1}{(2j+1)^2}} &= \frac{225}{518} \end{aligned} \quad (11.31)$$

From eqn. (11.10) we have:

$$\begin{aligned} a_1 &= 3 \left[1 - \frac{3}{-\frac{494}{497} \left(1 - \frac{1}{p}\right) \times 5 + 3} \right] \frac{225}{518} = \frac{675}{518} \left[\frac{-\frac{474}{497} \left(1 - \frac{1}{p}\right) \times 5}{-\frac{474}{497} \left(1 - \frac{1}{p}\right) \times 5 + 3} \right] = \frac{3375}{518} \left[\frac{-\frac{474}{497} \left(1 - \frac{1}{p}\right)}{-\frac{474}{497} \left(1 - \frac{1}{p}\right) \times 5 + 3} \right] \\ a_1 &= \left[\frac{-\frac{474}{497} \left(1 - \frac{1}{p}\right)}{-\frac{11692}{15975} \left(1 - \frac{1}{p}\right) + \frac{518}{1125}} \right] \end{aligned} \quad (11.32)$$

From eqn. (11.11) we have:

$$a_2 = \frac{3}{-\frac{474}{497}\left(1-\frac{1}{p}\right)+\frac{3}{5}} \times \frac{225}{518} = \frac{3}{-\frac{518}{225} \times \frac{474}{497}\left(1-\frac{1}{p}\right)+\frac{3}{5} \times \frac{518}{225}} = \frac{1}{-\frac{11692}{15975}\left(1-\frac{1}{p}\right)+\frac{518}{1125}} \quad (11.33)$$

We use the expression by Dinsdale (1991):

$$D = \frac{518}{1125} + \frac{11692}{15975} \left(\frac{1}{p} - 1 \right) \quad (11.34)$$

We insert eqn. (11.34) into (11.32) and (11.33) to arrive at:

$$a_1 = \frac{474}{497} \left(\frac{1}{p} - 1 \right) \frac{1}{D} \quad (11.35)$$

$$a_2 = \frac{1}{D} \quad (11.36)$$

We evaluate the last term in eqn. (11.30) by inserting (11.35) and (11.36):

$$\frac{949}{5400} a_1^{-1} - \frac{3271}{31500} a_2 = \frac{949}{5400} \times \frac{474}{497} \left(\frac{1}{p} - 1 \right) \frac{1}{D} - 1 - \frac{3271}{31500} \times \frac{1}{D} = \frac{1}{D} \left\{ \frac{949}{5400} \times \frac{474}{497} \left(\frac{1}{p} - 1 \right) - D - \frac{3271}{31500} \right\}$$

Next insert eqn. (11.34) for D in the parenthesis term:

$$\begin{aligned} \frac{949}{5400} a_1^{-1} - \frac{3271}{31500} a_2 &= \frac{1}{D} \left\{ \frac{449826}{2683800} \left(\frac{1}{p} - 1 \right) - \frac{518}{1125} - \frac{11692}{15975} \left(\frac{1}{p} - 1 \right) - \frac{3271}{31500} \right\} \\ \frac{949}{5400} a_1^{-1} - \frac{3271}{31500} a_2 &= \frac{1}{D} \left\{ \frac{449826}{2683800} \left(\frac{1}{p} - 1 \right) - \frac{518}{1125} - \frac{11692}{15975} \left(\frac{1}{p} - 1 \right) - \frac{3271}{31500} \right\} \\ \frac{949}{5400} a_1^{-1} - \frac{3271}{31500} a_2 &= \frac{1}{D} \left\{ \frac{74971}{447300} \left(\frac{1}{p} - 1 \right) - \frac{518}{1125} - \frac{11692}{15975} \left(\frac{1}{p} - 1 \right) - \frac{3271}{31500} \right\} \\ \frac{949}{5400} a_1^{-1} - \frac{3271}{31500} a_2 &= \frac{1}{D} \left\{ \left(\frac{74971}{447300} - \frac{11692}{15975} \right) \frac{1}{p} - \frac{74971}{447300} - \frac{518}{1125} + \frac{11692}{15975} - \frac{3271}{31500} \right\} \\ \frac{949}{5400} a_1^{-1} - \frac{3271}{31500} a_2 &= \frac{1}{D} \left\{ -\frac{79}{140} \frac{1}{p} - \frac{316043775}{503212500} + \frac{316043775}{503212500} \right\} = -\frac{1}{D} \frac{79}{140} \frac{1}{p} \end{aligned} \quad (11.37)$$

Insert eqn. (11.37) and (11.32) into (11.30):

$$g(\tau \leq 1) = -\frac{474}{497} \left(\frac{1}{p} - 1 \right) \frac{1}{D} \left\{ \frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right\} + \tau^{-1} \left\{ -\frac{1}{D} \frac{79}{140} \frac{1}{p} \right\} \quad (11.38)$$

The Helmholtz energy is than:

$$A^\lambda = n_a \cdot g(\tau) \cdot RT \ln(1 + \beta) \quad (11.5)$$

$$g(\tau \leq 1) = -\frac{474}{497} \left(\frac{1}{p} - 1 \right) \frac{1}{D} \left\{ \frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right\} + \tau^{-1} \left\{ -\frac{1}{D} \frac{79}{140} \frac{1}{p} \right\} \quad (11.38)$$

Comparing with Dinsdale (1991) we have:

$$g(\tau \leq 1) = g(\text{Calphad}, \tau \leq 1) - 1 \quad (11.39)$$

The reason for the difference is that in the Calphad expressions the magnetic entropy at zero Kelvin is negative, violating the 3rd law. That is more clearly seen in the Calphad expression above the critical temperature:

B. For temperatures above the critical temperature we have with eqn. (11.7):

Taking 3 terms in (11.7):

$$g(\tau > 1) = -1 + \frac{2a_2}{n} \left\{ \frac{\tau^{-n}}{-n+1} + \frac{\tau^{-3n}}{9(-3n+1)} + \frac{\tau^{-5n}}{25(-5n+1)} \right\}$$

We insert $n=5$:

$$g(\tau > 1) = -1 - a_2 \left\{ \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right\}$$

Next insert eqn. (11.36):

$$g(\tau > 1) = -1 - \frac{1}{D} \left\{ \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right\} \quad (11.40)$$

The Helmholtz energy becomes:

$$A^\lambda = n_a \cdot \left\{ -1 - \frac{1}{D} \left\{ \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right\} \right\} \cdot RT \ln(1 + \beta) \quad (11.41)$$

At infinite temperature we have:

$$\lim_{\tau \rightarrow \infty} A^\lambda = -n_a RT \ln(1 + \beta) \quad (11.42)$$

Eqn. (11.41) is the same result as the general result, eqn. (11.27).

Note that by comparing Dinsdale (1991):

$$g(\text{Calphad}, \tau > 1) = -\frac{1}{D} \left\{ \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right\} \quad (11.43)$$

$$g(\tau > 1) = g(\text{Calphad}, \tau > 1) - 1 \quad (11.44)$$

Eqn. (11.44) is consistently the same result as (11.39). When the Calphad expression by Dinsdale (1991), eqn. (11.43) is used we see that the magnetic contribution to Helmholtz energy is zero at infinite temperature contrasted to the quantum mechanical result, see e.g. Wu et al. (2009).

Note:

The Calphad formalism cannot be combined with the vibrational formalism programmed in 'me' because the magnetic contribution to entropy is negative at $T=0$, resulting in a negative total

entropy at $T=0$ when all physical contributions are summed. To repair the Calphad formalism such that the 3rd law of thermodynamics is obeyed requires:

$$S^{\lambda,corrected} = S^{\lambda}(\text{Calphad}) + n_a R \ln(1 + \beta)$$

$$A^{\lambda,corrected} = n_a \cdot [g(\text{Calphad}, \tau) - 1] \cdot RT \ln(1 + \beta)$$

The corrected model has been applied to Fe_2SiO_4 (fayalite) by Jacobs and de Jong (2009), see also section 14 of this manual.

11.4. Derivation of the constants a_1 and a_2 , eqn. (11.10) and (11.11)

We start from eqn. (11.3) and (11.4) for the isochoric heat capacity. Next we derive the entropy by integration. The constants a_1 and a_2 are determined by demanding that the entropy at infinite temperature equals $+n_a R \ln(1+\beta)$ in accordance with quantum mechanics, see e.g. Wu et al (2009).

We use the thermodynamic definition:

$$\left(\frac{\partial S^\lambda}{\partial T}\right)_V = \frac{C_V^\lambda}{T} \quad \left(\frac{\partial S^\lambda}{\partial \tau}\right)_V = \frac{C_V^\lambda}{\tau} \quad (11.45)$$

Integrating (11.3) to temperature gives:

$$S^\lambda(\tau \leq 1) = \int_0^\tau \frac{C_V^\lambda}{\tau} d\tau = 2a_1 n_a R \sum_{j=0}^{\infty} \frac{\tau^{(2j+1)m}}{m(2j+1)^2} \ln(1+\beta) \quad (11.46)$$

$$S^\lambda(\tau = 1) = \frac{2a_1}{m} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} n_a R \ln(1+\beta) \quad (11.47)$$

For temperatures above the critical temperature we find by integration of eqn. (11.4) between 1 and τ and adding eqn. (11.47):

$$S^\lambda(\tau > 1) = \int_0^1 \frac{C_V^\lambda}{\tau} d\tau + \int_1^\tau \frac{C_V^\lambda}{\tau} d\tau$$

$$S^\lambda(\tau > 1) = \left\{ \frac{2a_1}{m} \sum_{j=1}^{\infty} \frac{1}{(2j+1)^2} - \frac{2a_2}{n} \sum_{j=0}^{\infty} \frac{\tau^{-(2j+1)n} - 1}{(2j+1)^2} \right\} n_a R \ln(1+\beta) \quad (11.48)$$

At infinite temperature eqn. (11.48) with the constraint gives:

$$\lim_{T \rightarrow \infty} S^\lambda = 2 \left(\frac{a_1}{m} + \frac{a_2}{n} \right) \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} n_a R \ln(1+\beta) \equiv n_a R \ln(1+\beta) \quad (11.49)$$

Eqn. (11.49) gives:

$$\frac{a_1}{m} + \frac{a_2}{n} = \frac{1}{2} \frac{1}{\sum_{j=0}^{\infty} \frac{1}{(2j+1)^2}} \equiv Q \quad (11.50)$$

With eqn. (11.50) we can express a_2 in a_1 :

$$a_2 = n \left(Q - \frac{a_1}{m} \right) \quad (11.51)$$

$$Q = \frac{1}{2 \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2}} \quad (11.52)$$

From the definition of 'p', eqn. (11.14), and integration of (11.3), (11.4) we find:

$$p = \frac{\int_0^{\infty} C_V^\lambda d\tau}{\int_0^{\infty} C_V^\lambda d\tau} \quad (11.53)$$

$$\int_0^1 C_V^\lambda d\tau = 2a_1 \sum_{j=0}^{\infty} \frac{1}{(2j+1)[(2j+1)m+1]} n_a R \ln(1+\beta) \quad (11.54)$$

$$\int_1^{\infty} C_V^\lambda d\tau = -2a_2 \sum_{j=0}^{\infty} \frac{1}{(2j+1)[-(2j+1)n+1]} n_a R \ln(1+\beta) \quad (11.55)$$

$$p = - \frac{a_2 \sum_{j=0}^{\infty} \frac{1}{(2j+1)[-(2j+1)n+1]}}{a_1 \sum_{j=0}^{\infty} \frac{1}{(2j+1)[(2j+1)m+1]} - a_2 \sum_{j=0}^{\infty} \frac{1}{(2j+1)[-(2j+1)n+1]}} \quad (11.56)$$

We insert the abbreviations (11.12) and (11.13) defined in section 11.1 into eqn. (11.56):

$$s_1 = \sum_{j=0}^{\infty} \frac{1}{(2j+1)[(2j+1)m+1]} \quad (11.12)$$

$$s_2 = \sum_{j=0}^{\infty} \frac{1}{(2j+1)[-(2j+1)n+1]} \quad (11.13)$$

$$p = - \frac{k_2 s_2}{k_1 s_1 - k_2 s_2} \quad (11.57)$$

Next we combine eqn. (11.57) with eqn. (11.51) to express a_1 and a_2 in p , n , and m :

$$a_1 = mQ \left[1 - \frac{m}{\frac{s_2}{s_1} \left(1 - \frac{1}{p} \right) n + m} \right] \quad (11.58)$$

$$a_2 = \frac{mQ}{\frac{s_2}{s_1} \left(1 - \frac{1}{p} \right) + \frac{m}{n}} \quad (11.59)$$

$$Q = \frac{1}{2 \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2}} \quad (11.60)$$

Expressions (11.58) is identical with eqn. (11.10) and expression (11.59) is identical with eqn. (11.11) as we wanted to proof.

11.5. Example of input in 'me'

An example of a part of an input file for FeO is given below. Lines dealing with magnetic contributions to thermodynamic properties are marked in blue.

For iron silicates magnetism often appears in combination with crystal field. An example of input for Fe₂SiO₄ (fayalite) requiring more terms in the McLaurin expression is given in section 14. Some notes are given in section 14.5 for obtaining physical contributions to thermodynamic properties.

```
#
FeO (* Name of the substance *)
 71.846000 (* Mass of the substance in gr/mol *)
 2.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-2.88285665810131E+005 (* Static lattice energy in J/mol *)
 1.21895288889273E-005 (* Volume/m3/mol at zero K and zero Pa *)
 1.20885034259776E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
 2 (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice *)
 4 (* Order of Birch-Murnaghan EoS of the static lattice *)
 1.832637000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
-2.937701000000000E+000 (* --- 1st pressure derivative coefficient of the static lattice ...*)
 3.027441000000000E+000 (* --- 2nd pressure derivative coefficient of the static lattice ...*)
 6.211468000000000E+010 (* Static lattice shear modulus/Pa at zero Pa *)
-4.643524000000000E+000 (* --- 1st pressure derivative coefficient of the static lattice ...*)
-2.252377000000000E+001 (* --- 2nd pressure derivative coefficient of the static lattice ...*)
-2.090609000000000E+000 (* Vibrational parameter of the shear modulus *)
 0 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order...
 1 (* 0=No magnetic contribution, 1=magnetic contribution *)
 51 (* Magnetic: number of terms in the MacLaurin series expansion >2 *)
 2.800000000000000E-001 (* Magnetic: Ratio Energy(tau>1)/total Energy for magnetic transition
 1.910156000000000E+002 (* Magnetic: Critical temperature Tc *)
 4.000000000000000E+000 (* Magnetic: magnetic moment in Bohr magneton *)
 3.000000000000000E+000 (* Magnetic: exponent (m) in Inden's (1981) expression for Cv below Tc
 5.000000000000000E+000 (* Magnetic: exponent (n) in Inden's (1981) expression for Cv above Tc
 1.000000000000000E+000 (* Magnetic: number of magnetic atoms per formula unit *)
 1 (* Free electron gas model *)
# Cv=a*T*(V/V0)^gamma_el
 0.000000000000000E+000 (* Electronic Gruneisen parameter, gamma_el *)
 3.869000000000000E-003 (* Electronic coefficient, a, in J/mol/K/K *)
 0 (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984) *)
 0 (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &...*)
.
.
...etc
```

Electronic contributions

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This part of the manual contains model descriptions for the electronic contribution. Three models are programmed in '*me*'. The first one is the free electron gas model. The second one is an extended free electron gas model, including the free electron gas model, and which is used for parameterizing the heat capacity resulting from electron-phonon coupling, such as is the case for platinum and nickel. The last case is the crystal-field model, required for representing low-temperature heat capacity of fayalite Fe_2SiO_4 .

The thermodynamic properties calculated from these methods are considered as contributions, added to other physical contributions of the Gibbs or Helmholtz energy, such as static, vibrational, and electronic contributions.

12 Free electron gas model

The free electron gas model is discussed in many textbooks, eg in Gopal (1966) or Kittel (1996). For elements such as aluminium and copper this model is quite well applicable. For other elements such as gold, platinum and nickel it is less accurate. The effect of the electronic contribution to heat capacity is that isochoric heat capacity of an element breaks through the duLong-Petit limit of 3 times the gas constant at high temperature, such as depicted in Figure 12.1.

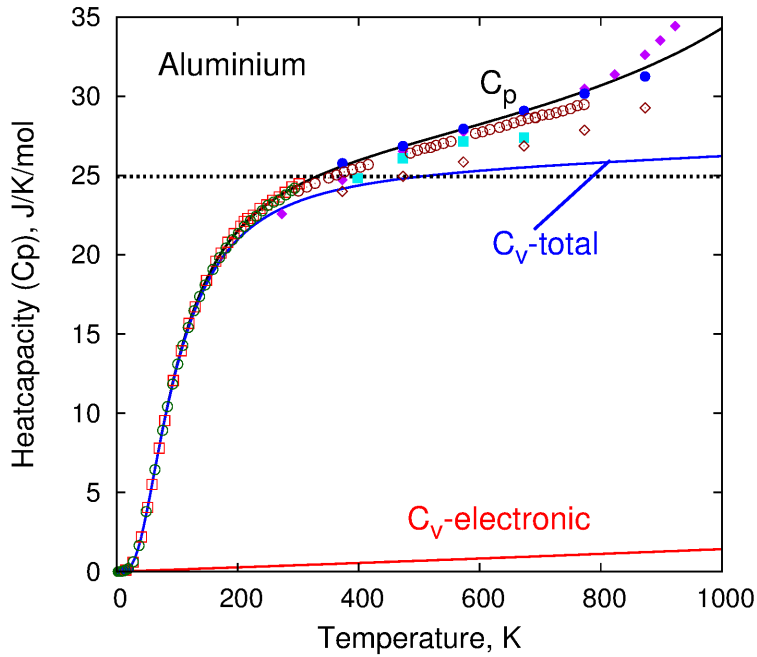


Figure 12.1. Isobaric heat capacity of aluminium calculated by *'me'* is plotted as the black curve. The isochoric heat capacity including lattice vibrations and electronic contribution is plotted in blue. The electronic contribution to isochoric heat capacity is plotted in red. The duLong-Petit limit to which the vibrational contribution to isochoric heat capacity converges is represented by the dashed line. References are given in Jacobs et al. (2013) and Jacobs and Schmid-Fetzer (2010)

Expressions for electronic contribution to thermodynamic properties are given below. The value for γ_{el} is usually taken to be $2/3$.

$$\text{Helmholtz energy:} \quad A^{el} = -\frac{\beta_{el}}{2} \left(\frac{V}{V_0} \right)^{\gamma_{el}} T^2 \quad (12.1)$$

$$\text{Energy:} \quad U^{el} = \frac{\beta_{el}}{2} \left(\frac{V}{V_0} \right)^{\gamma_{el}} T^2 \quad (12.2)$$

$$\text{Entropy:} \quad S^{el} = \beta_{el} \left(\frac{V}{V_0} \right)^{\gamma_{el}} T \quad (12.3)$$

$$\text{Isochoric heat capacity:} \quad C_v^{el} = \beta_{el} \left(\frac{V}{V_0} \right)^{\gamma_{el}} T \quad (12.4)$$

$$\text{Pressure:} \quad P^{el} = \frac{\beta_{el} \gamma_{el}}{2V} \left(\frac{V}{V_0} \right)^{\gamma_{el}} T^2 \quad (12.5)$$

$$\text{Isothermal bulk modulus: } K^{el} = -\frac{\beta_{el}\gamma_{el}(\gamma_{el}-1)}{2V}\left(\frac{V}{V_0}\right)^{\gamma_{el}} T^2 \quad (12.6)$$

Isochoric temperature derivative of electronic pressure:

$$: \left(\frac{\partial P^{el}}{\partial T}\right)_V^{el} = \frac{\beta_{el}\gamma_{el}}{V}\left(\frac{V}{V_0}\right)^{\gamma_{el}} T \quad (12.7)$$

In file **demo.mef** aluminium is present and a part of the input file is given in Table 12.1. Figure 12.1 shows for a 30-Einstein model the heat capacity calculated with *'me'*.

Table 12.1. Part of the input file for aluminium in **demo.mef**. Lines describing the free electron gas model are coloured in blue.

```
#
<Al-30E>                (* Name of the substance *)
 26.981540              (* Mass of the substance in gr/mol *)
 1.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-8.32458684417284E+003 (* Static lattice energy in J/mol *)
 9.87304836203274E-006 (* Volume/m3/mol at zero K and zero Pa *)
 9.77516605718424E-006 (* Volume/m3/mol of the static lattice at zero Pa *)
 2                      (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice
 5                      (* Order of Birch-Murnaghan EoS of the static lattice *)
 8.180659000000000E+010 (* Static lattice bulk modulus/Pa at zero Pa *)
 8.132380000000000E-001 (* --- 1st pressure derivative coefficient of the static lattice bulk
-3.929825000000000E+000 (* --- 2nd pressure derivative coefficient of the static lattice bulk
 5.784287000000000E+000 (* --- 3rd pressure derivative coefficient of the static lattice bulk
 3.091332000000000E+010 (* Static lattice shear modulus/Pa at zero Pa *)
-8.514126000000000E-001 (* --- 1st pressure derivative coefficient of the static lattice shea
 0.000000000000000E+000 (* --- 2nd pressure derivative coefficient of the static lattice shea
 0.000000000000000E+000 (* --- 3rd pressure derivative coefficient of the static lattice shea
 1.784524000000000E+000 (* Vibrational parameter of the shear modulus *)
 0                      (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order
 0                      (* 0=No magnetic contribution, 1=magnetic contribution *)
 1                      (* Free electron gas model *)
# Cv=a*T*(V/V0)^gamma_el
 6.666667000000000E-001 (* Electronic Gruneisen parameter, gamma_el *)
 1.350000000000000E-003 (* Electronic coefficient, a, in J/mol/K/K *)
 0                      (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984)*)
 0                      (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &...*)
# Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
 30                     (* Number of Einstein modes *)
.
.
...etc
```


13 Extended free electron gas model

Tsuchiya and Kawamura (2002) showed by ab initio calculations that the electronic isochoric heat capacity of gold and platinum behaves non-linearly with temperature. Therefore the simple free electron gas model of section 12 is not applicable. In Jacobs et al. (2013) a simple empirical parameterization of the electronic heat capacity is given, which appears to be applicable to gold and nickel too.

A function enabling a proper description of the isochoric heat capacity behavior is given by Jacobs et al. (2013) as:

$$C_V^{el} = \left\{ \sum_{i=1}^3 a_i T^i e^{-b_i T} + c_1 T + c_2 \left(1 - \frac{1}{c_3 T + 1} \right) \right\} \left(\frac{V}{V_0} \right)^{\gamma_{el}} \quad (13.1)$$

$$\left(\frac{dC_V^{el}}{dT} \right)_V = \left\{ \sum_{i=1}^3 a_i (i - b_i T) T^{i-1} e^{-b_i T} + c_1 + \frac{c_2 c_3}{(c_3 T + 1)^2} \right\} \left(\frac{V}{V_0} \right)^{\gamma_{el}} \quad (13.2)$$

The first term in eqn. (13.1) describes the curvature in the low temperature regime. The other terms describe the high temperature heat capacity behavior. The last term is needed because the high temperature heat capacity data extrapolated to 0 K indicate a positive intercept for Pt and Ni as can be deduced from eqn. (13.2). V_0 denotes the volume at zero Kelvin, zero pressure, V the volume at (P, T) , and γ_{el} the electronic Grüneisen parameter, which equals 2/3 in the free electron gas theory. Some useful relations to constrain the coefficients in eqn (13.1) are:

$$\lim_{T \rightarrow 0} \left(\frac{dC_V^{el}}{dT} \right)_V = (a_1 + c_1 + c_2 c_3) \left(\frac{V}{V_0} \right)^{\gamma_{el}} = a_1 + c_1 + c_2 c_3 \quad (13.3a)$$

$$\lim_{T \rightarrow \infty} C_V^{el} = (c_1 T + c_2) \left(\frac{V}{V_0} \right)^{\gamma_{el}} \quad (13.3b)$$

13.1. Thermodynamic properties

From the isochoric heat capacity (13.1) one derives by integration the entropy and Helmholtz energy and subsequently the contributions to pressure, bulk modulus and thermal expansivity. In the derivation we use:

$$\int_0^T T e^{-zT} dT = -\frac{T}{z} e^{-zT} + \frac{1}{z^2} (1 - e^{-zT}) \quad (13.4)$$

Integrating heat capacity to temperature gives entropy. The entropy is obtained from isochoric heat capacity:

$$\left(\frac{\partial S^{el}}{\partial T} \right)_V = \left\{ \sum_{i=1}^3 a_i e^{-b_i T} T^{i-1} + c_1 + \frac{c_2}{T} \left(1 - \frac{1}{c_3 T + 1} \right) \right\} \left(\frac{V}{V_0} \right)^{\gamma_{el}} \quad (13.5)$$

Or:

$$\left(\frac{\partial S^{el}}{\partial T}\right)_V = \left\{ \sum_{i=1}^3 a_i e^{-b_i T} T^{i-1} + c_1 + \frac{c_2 c_3}{c_3 T + 1} \right\} \left(\frac{V}{V_0}\right)^{\gamma_{el}} \quad (13.6)$$

Electronic entropy

Integration of eqn. (13.6) gives:

$$S^{el} = \left\{ \frac{a_1}{b_1} (1 - e^{-b_1 T}) - \frac{a_2}{b_2} T e^{-b_2 T} + \frac{a_2}{b_2^2} (1 - e^{-b_2 T}) - \frac{a_3}{b_3} T^2 e^{-b_3 T} + \frac{2a_3}{b_3} \left[-\frac{T}{b_3} e^{-b_3 T} + (1 - e^{-b_3 T}) \frac{1}{b_3^2} \right] + c_1 T + c_2 \ln(c_3 T + 1) \right\} \left(\frac{V}{V_0}\right)^{\gamma_{el}} \quad (13.7)$$

Electronic Helmholtz energy

Integration of eqn. (13.7) gives:

$$A^{el} = \left\{ -\frac{a_1}{b_1} T + \frac{a_1}{b_1^2} (1 - e^{-b_1 T}) - \frac{a_2 T}{b_2^2} (1 + e^{-b_2 T}) + \frac{2a_2}{b_2^3} (1 - e^{-b_2 T}) + \frac{a_3}{b_3} \left[-\frac{T^2}{b_3} e^{-b_3 T} + \frac{2}{b_3^2} \left(-T e^{-b_3 T} + \frac{1}{b_3} (1 - e^{-b_3 T}) \right) \right] - \frac{2a_3 T}{b_3^3} [e^{-b_3 T} + 1] + \frac{1}{2} c_1 T^2 - \frac{c_2}{c_3} [(c_3 T + 1) \ln(c_3 T + 1) - c_3 T] \right\} \left(\frac{V}{V_0}\right)^{\gamma_{el}} \quad (13.8)$$

Electronic pressure

From eqn. (13.7):

$$P^{el} = -\frac{\gamma_{el}}{V} A^{el} \quad (13.9)$$

Electronic bulk modulus

From eqn. (13.9):

$$K^{el} = \frac{\gamma_{el}(\gamma_{el} - 1)}{V} A^{el} \quad (13.10)$$

Temperature derivative of electronic pressure

From eqn. (13.10):

$$\left(\frac{\partial P^{el}}{\partial T}\right)_V = \frac{\gamma_{el}}{V} S^{el} \quad (13.11)$$

13.2. 'me' input file for Platinum

A part of the input file for **'me'** is given in Table 13.1 and also present in file [demo.mef](#). Lines containing coefficients describing the electronic contribution are coloured in blue. The coefficients, describing the combined effect of electronic and electron-phonon coupling on thermodynamic properties, were obtained by Jacobs et al. (2013). That was achieved by subtracting from the isobaric heat capacity the contributions of the dilation and lattice vibrations. To obtain the

electronic heat capacity including the electron-phonon coupling use was made of the electronic heat capacity predicted by Tsuchiya and Kawamura (2002) in which no electron-phonon coupling was taken into account, shown as the blue curve in Figure 13.1. Grimvall's (1968) method was employed to derive the electron-phonon coupling for 30 Einstein frequencies in the VDoS, which added to the blue curve results in the black curve.

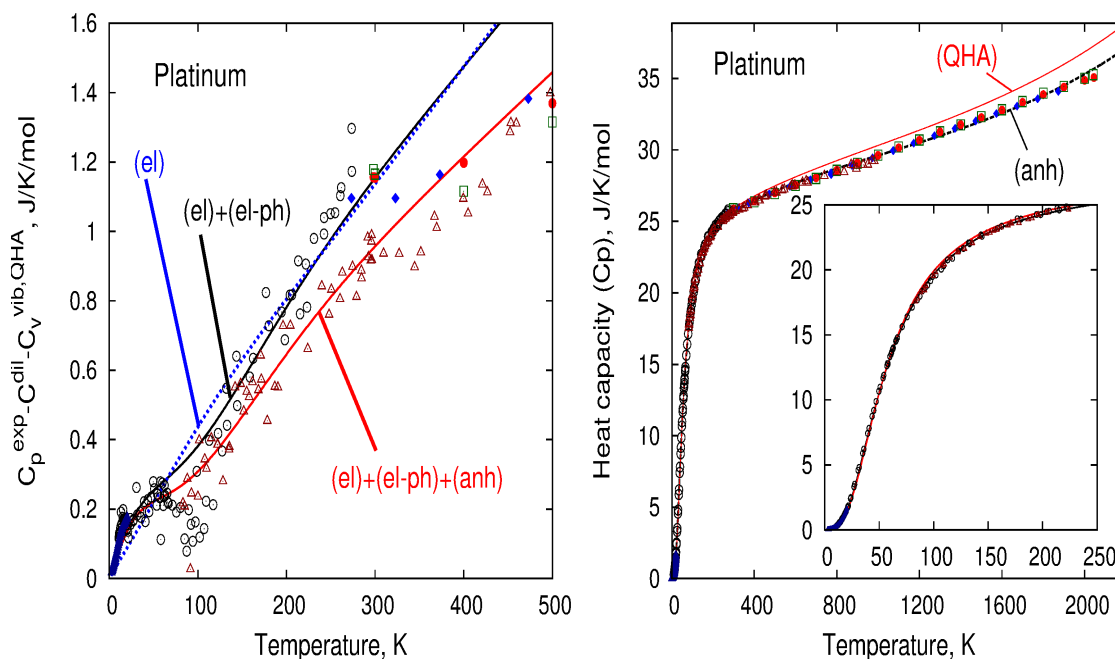


Figure 13.1. Left: Curves at 1 bar for platinum were obtained by adding electronic (el), electron-phonon (el-ph) and intrinsic anharmonic (anh) effects in the isochoric heat capacity. To obtain the electronic contribution to isochoric heat capacity, the dilation contribution and vibrational isochoric heat capacity calculated in the quasi-harmonic approximation were subtracted from the experimental isobaric heat capacity. Data are from Jaeger & Rosenbohm (1939), solid diamond, Clusius et al. (1957), open circle, Kendall et al. (1962), open square, Berg (1969), solid triangle, Yokokawa & Takahashi (1979), open triangle, Barin (1989), solid circle. Right: isobaric heat capacity. For references see Jacobs et al. (2013).

Intrinsic anharmonicity was established by using high-temperature heat capacity and Hugoniot data, and by adding this effect to the black curve the red curve in Figure 13.1 is obtained. This way an accurate description for low-temperature heat capacity and room temperature entropy for platinum was achieved. The coefficients in the input file of Table 13.1 describe the isochoric heat capacity of the black curve. Intrinsic anharmonicity is described by coefficient a_0 in Table 13.1.

Table 13.1. Part of the input file constructed from `demo.mef` for use in `'me'` for platinum. Coefficients describing the electronic contribution to the Helmholtz energy are given on the blue coloured lines.

```
#
<Platinum>          (* Name of the substance *)
195.080000          (* Mass of the substance in gr/mol *)
1.0000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-8.13459742018308E+003 (* Static lattice energy in J/mol *)
9.03740542850234E-006 (* Volume/m3/mol at zero K and zero Pa *)
9.01696059323866E-006 (* Volume/m3/mol of the static lattice at zero Pa *)
1                  (* l=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice
3                  (* Order of Vinet EoS of the static lattice *)
```

```

2.899927000000000E+011      (* Static lattice bulk modulus/Pa at zero Pa *)
5.149613000000000E+000      (* Pressure derivative of the static lattice bulk modulus at zero Pa
0                             (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order
0                             (* 0=No magnetic contribution, 1=magnetic contribution *)
2                             (* Extended free electron gas model: electron-phonon coupling *)
# Cv=(a1*T*exp(-b1*T)+a2*T^2*exp(-b2*T)+a3*T^3*exp(-b3*T)+c1*T+c2*(1-1/(c3*T+1)))*(V/V0)^gamma_el
6.666667000000000E-001      (* Electronic Gruneisen parameter, gamma_el *)
#   a           b           c
# -----
1 -2.629956E-002  9.626541E-003  1.000000E-003
2  3.224574E-004  4.260242E-002  2.259624E+000
3 -1.667092E-007  7.075324E-003  1.411277E-002
0                             (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984)*)
0                             (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &...*)
# Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004):
30                            (* Number of Einstein modes *)
1                             (* 1=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by
Stixrude & Lithgow-Bertelloni, 2005 *)
# j   Theta/K   Fraction      Gamma      Mode_m(q)   Gamma_inf   a0           z
# -----
1     7.2972    1.600000000E-004  2.6822100  2.7720800   0.6666600   2.580000E-005  0.0000000
2    16.8142    3.500000000E-004  2.6822100  2.7720800   0.6666600   2.580000E-005  0.0000000
3    26.3312    9.100000000E-004  2.6822100  2.7720800   0.6666600   2.580000E-005  0.0000000
4    35.8482    2.080000000E-003  2.6822100  2.7720800   0.6666600   2.580000E-005  0.0000000
.
.
. etc...

```

14 Crystal-Field model

In this section Fe_2SiO_4 (fayalite) is used as example to demonstrate the crystal field effect on thermodynamic properties. Fayalite is a substance in which oxygen atoms octahedrally surround the Fe atoms. The Fe atom has 6 electrons in its 3d orbitals. To minimize the energy the lobes of the d_{xy} , d_{xz} , d_{yz} Fe orbitals point in between the O-atoms and the $d_{x^2-y^2}$ and d_{z^2} point towards the O-atoms. Because there is more electron repulsion in the last two levels, these are higher in energy than the first three levels. The first three levels are called the t_{2g} and the other two the e_g levels. The configuration of the electrons is high-spin because it takes less energy to promote an electron from t_{2g} to e_g than it takes to pair the sixth electron with another one. Because spin-orbit coupling is present each level is split further into 5 levels and we get 25 levels in total (15 in the lower t_{2g} and 10 in the higher e_g levels).

The thermodynamic properties for an m -level system (electrons may occupy m quantized energy levels) are derived using statistical mechanics. The partition function Z is written:

$$Z = \sum_{j=1}^m g_j \exp\left(-\frac{\varepsilon_j}{kT}\right) \quad (14.1)$$

In eqn. (14.1) g_i denotes the degeneracy of a level i with energy ε_i , k the Boltzmann constant, and T the temperature. The ground state is taken as level 1 and its energy is taken to be zero. In sections 14.2 and 14.3 it is shown that the problem arises with eqn. (14.1) that the entropy is not zero when the degeneracy of the ground state is not equal to one. This is the case when the data of Aronson et al. (2007) for fayalite are used. This deficiency is repaired in section 14.3. The partition function is written as:

$$Z = \frac{\sum_{j=1}^m g_j \exp\left(-\frac{\varepsilon_j}{kT}\right)}{g_1 \exp\left(-\frac{\varepsilon_1}{kT}\right)} \quad (14.2)$$

To make equations shorter, we take eqn. (14.1) as a starting point for developing the expressions for the thermodynamic properties. Correcting the entropy such that the 3rd law is obeyed, is simply achieved by substituting g_i/g_1 for g_i in eqn. (14.1) resulting in the partition function of eqn. (14.2) and next taking $\varepsilon_1=0$.

Using statistical mechanics the electronic contribution to Helmholtz energy, A^{el} is given by:

$$A^{el} = -kT \ln Z \quad (14.3)$$

Using eqn. (14.1) for the partition function, the Helmholtz energy for m energy levels per one atom Fe in fayalite becomes:

$$A^{el} = -kT \ln \left(\sum_{j=1}^m g_j \exp\left(-\frac{\varepsilon_j}{kT}\right) \right) \quad (14.4)$$

In the case that we have n atoms per formula unit that may have crystal field splitting, we write for one mole of formula unit:

$$A^{el} = -nRT \ln \left(\sum_{j=1}^m g_j \exp \left(-\frac{\varepsilon_j}{kT} \right) \right) \quad (14.5)$$

For Fe_2SiO_4 (fayalite) the value of n equals two. We use a shorter notation in eqn. (14.5) by setting:

$$A^{el} = -nRT \ln \left(\sum_{j=1}^m g_j e^{-x_j} \right) \quad (\text{see also 14.38}) \quad (14.6a)$$

$$x_j = \frac{\varepsilon_j}{kT} \quad (14.6b)$$

To derive thermodynamic properties from the Helmholtz energy contribution, we make use of the expressions:

$$\left(\frac{\partial x_j}{\partial T} \right)_V = -\frac{x_j}{T} \quad (14.7)$$

$$\left(\frac{\partial x_j}{\partial V} \right)_T = -\frac{\gamma_j x_j}{V} \quad (14.8)$$

$$\gamma_j = - \left(\frac{\partial \ln \varepsilon_j}{\partial \ln V} \right)_T \quad (14.9)$$

In eqn. (14.9), γ_j denotes the Grüneisen parameter of the j^{th} energy level. By differentiation of the Helmholtz energy to volume and temperature we obtain from eqn. (14.6a):

$$S^{el} = - \left(\frac{\partial A^{el}}{\partial T} \right)_V = nR \ln \left(\sum_{j=1}^m g_j e^{-x_j} \right) + nR \frac{\sum_{j=1}^m g_j x_j e^{-x_j}}{\sum_{j=1}^m g_j e^{-x_j}} \quad (\text{see also 14.40}) \quad (14.10)$$

$$U^{el} = A^{el} + TS^{el} = nRT \frac{\sum_{j=1}^m g_j x_j e^{-x_j}}{\sum_{j=1}^m g_j e^{-x_j}} \quad (14.11)$$

$$C_v^{el} = \left(\frac{\partial U^{el}}{\partial T} \right)_V = nR \left\{ \frac{\sum_{j=1}^m g_j x_j^2 e^{-x_j}}{\sum_{j=1}^m g_j e^{-x_j}} - \left(\frac{\sum_{j=1}^m g_j x_j e^{-x_j}}{\sum_{j=1}^m g_j e^{-x_j}} \right)^2 \right\} \quad (14.12)$$

$$P^{el} = - \left(\frac{\partial A^{el}}{\partial V} \right)_T = \frac{nRT}{V} \frac{\sum_{j=1}^m g_j \gamma_j x_j e^{-x_j}}{\sum_{j=1}^m g_j e^{-x_j}} \quad (14.13)$$

$$K^{el} = -V \left(\frac{\partial P^{el}}{\partial V} \right)_T = \frac{nRT}{V} \left\{ \frac{\sum_{j=1}^m g_j \gamma_j x_j e^{-x_j}}{\sum_{j=1}^m g_j e^{-x_j}} - \left[\frac{\sum_{j=1}^m g_j \gamma_j^2 (x_j^2 - x_j) e^{-x_j}}{\sum_{j=1}^m g_j e^{-x_j}} - \left(\frac{\sum_{j=1}^m g_j \gamma_j x_j e^{-x_j}}{\sum_{j=1}^m g_j e^{-x_j}} \right)^2 \right] \right\} \quad (14.14)$$

$$\left(\frac{\partial P^{el}}{\partial T} \right)_V = \frac{nR}{V} \left\{ \frac{\sum_{j=1}^m g_j \gamma_j x_j^2 e^{-x_j}}{\sum_{j=1}^m g_j e^{-x_j}} - \frac{\sum_{j=1}^m g_j \gamma_j x_j e^{-x_j} \sum_{j=1}^m g_j x_j e^{-x_j}}{\left(\sum_{j=1}^m g_j e^{-x_j} \right)^2} \right\} \quad (14.15)$$

Eqn. (14.15) is needed for calculating thermal expansivity by summing all isochoric temperature derivatives of the different thermophysical pressure contributions.

For evaluating eqn. (14.6a), (14.10-14.15) in program **'me'** we use:

$$\begin{aligned} Z_A &= \sum_{j=1}^m g_j e^{-x_j} & Z_p &= \sum_{j=1}^m g_j \gamma_j x_j e^{-x_j} \\ Z_S &= \sum_{j=1}^m g_j x_j e^{-x_j} & Z_K &= \sum_{j=1}^m g_j \gamma_j^2 (x_j^2 - x_j) e^{-x_j} \\ Z_{cv} &= \sum_{j=1}^m g_j x_j^2 e^{-x_j} & Z_{dpdt} &= \sum_{j=1}^m g_j \gamma_j x_j^2 e^{-x_j} \end{aligned} \quad (14.16)$$

With the definitions in (14.16), we obtain for thermodynamic properties:

$$A^{el} = -nRT \ln(Z_A) \quad (14.17)$$

$$S^{el} = nR \ln(Z_A) + nR \frac{Z_S}{Z_A} \quad (14.18)$$

$$U^{el} = nRT \frac{Z_S}{Z_A} \quad (14.19)$$

$$C_v^{el} = nR \left\{ \frac{Z_{cv}}{Z_A} - \left(\frac{Z_S}{Z_A} \right)^2 \right\} \quad (14.20)$$

$$P^{el} = \frac{nRT}{V} \frac{Z_p}{Z_A} \quad (14.21)$$

$$K^{el} = \frac{nRT}{V} \left\{ \frac{Z_p}{Z_A} - \left[\frac{Z_K}{Z_A} - \left(\frac{Z_p}{Z_A} \right)^2 \right] \right\} \quad (14.22)$$

$$\left(\frac{\partial P^{el}}{\partial T} \right)_V = \frac{nR}{V} \left\{ \frac{Z_{dpdt}}{Z_A} - \frac{Z_p Z_S}{Z_A^2} \right\} \quad (14.23)$$

14.1. Limiting values of thermodynamic properties: $T \rightarrow \infty$

When temperature goes to infinity, eqn. (14.6b) shows that x_j goes to zero. Inserting that into eqn. (14.6a) and (14.10-15) gives:

$$A^\infty = -nRT \ln \left(\sum_{j=1}^m g_j \right) \quad (14.24)$$

$$S^\infty = nR \ln \left(\sum_{j=1}^m g_j \right) + nR \frac{\sum_{j=1}^m g_j x_j}{\sum_{j=1}^m g_j} = nR \ln \left(\sum_{j=1}^m g_j \right) \quad (14.25)$$

$$U^\infty = nRT \frac{\sum_{j=1}^m g_j x_j}{\sum_{j=1}^m g_j} = nN_A \frac{\sum_{j=1}^m g_j \varepsilon_j}{\sum_{j=1}^m g_j} \quad (14.26)$$

$$C_V^\infty = nR \left\{ \frac{\sum_{j=1}^m g_j x_j^2}{\sum_{j=1}^m g_j} - \left(\frac{\sum_{j=1}^m g_j x_j}{\sum_{j=1}^m g_j} \right)^2 \right\} = 0 \quad (14.27)$$

$$P^\infty = \frac{nRT}{V} \frac{\sum_{j=1}^m g_j \gamma_j x_j}{\sum_{j=1}^m g_j} = \frac{nN_A}{V} \frac{\sum_{j=1}^m g_j \gamma_j \varepsilon_j}{\sum_{j=1}^m g_j} \quad (14.28)$$

$$K^\infty = \frac{nRT}{V} \left\{ \frac{\sum_{j=1}^m g_j \gamma_j x_j}{\sum_{j=1}^m g_j} - \left[\frac{\sum_{j=1}^m g_j \gamma_j^2 (x_j^2 - x_j)}{\sum_{j=1}^m g_j} - \left(\frac{\sum_{j=1}^m g_j \gamma_j x_j}{\sum_{j=1}^m g_j} \right)^2 \right] \right\} = \frac{nN_A}{V} \frac{\sum_{j=1}^m g_j \gamma_j \varepsilon_j - \sum_{j=1}^m g_j \gamma_j^2 \varepsilon_j}{\sum_{j=1}^m g_j} \quad (14.29)$$

$$\left(\frac{\partial P^{el}}{\partial T} \right)_V^\infty = \frac{nR}{V} \left\{ \frac{\sum_{j=1}^m g_j \gamma_j x_j^2}{\sum_{j=1}^m g_j} - \frac{\sum_{j=1}^m g_j \gamma_j x_j \sum_{j=1}^m g_j x_j}{\left(\sum_{j=1}^m g_j \right)^2} \right\} = 0 \quad (14.30)$$

14.2. Limiting values of thermodynamic properties: $T \rightarrow 0$

We make use of $\varepsilon_i=0$ for the ground state energy and that x_j is infinity at $T=0$, eqn. (14.6b). Thermodynamic properties derived from (14.6a) and (14.10-15) are:

$$\lim_{T \downarrow 0} A^{el} = -nRT \ln \left(g_1 e^{-x_1} + \sum_{j=2}^m g_j e^{-x_j} \right) = -nRT \ln \left(g_1 \exp\left(-\frac{\varepsilon_1}{kT}\right) + \sum_{j=2}^m g_j e^{-x_j} \right) = -nRT \ln(g_1) = 0 \quad (14.31)$$

$$\lim_{T \downarrow 0} S^{el} = nR \ln \left(g_1 \exp\left(-\frac{\varepsilon_1}{kT}\right) + \sum_{j=2}^m g_j e^{-x_j} \right) + nR \frac{g_1 \frac{\varepsilon_1}{kT} \exp\left(-\frac{\varepsilon_1}{kT}\right) + \sum_{j=2}^m g_j x_j e^{-x_j}}{g_1 \exp\left(-\frac{\varepsilon_1}{kT}\right) + \sum_{j=2}^m g_j e^{-x_j}} = nR \ln(g_1) \quad (14.32)$$

$$\lim_{T \downarrow 0} U^{el} = nRT \frac{g_1 \frac{\varepsilon_1}{kT} \exp\left(-\frac{\varepsilon_1}{kT}\right) + \sum_{j=2}^m g_j x_j e^{-x_j}}{g_1 \exp\left(-\frac{\varepsilon_1}{kT}\right) + \sum_{j=2}^m g_j e^{-x_j}} = nN_A \varepsilon_1 = 0 \quad (14.33)$$

$$\lim_{T \downarrow 0} C_v^{el} = 0 \quad (14.34)$$

$$\lim_{T \downarrow 0} P^{el} = \frac{nRT}{V} \frac{g_1 \gamma_1 \frac{\varepsilon_1}{kT} \exp\left(-\frac{\varepsilon_1}{kT}\right) + \sum_{j=2}^m g_j \gamma_j x_j e^{-x_j}}{g_1 \exp\left(-\frac{\varepsilon_1}{kT}\right) + \sum_{j=2}^m g_j e^{-x_j}} = 0 \quad (14.35)$$

$$\lim_{T \downarrow 0} K^{el} = \frac{nRT}{V} \left\{ \frac{g_1 \gamma_1 \frac{\varepsilon_1}{kT} \exp\left(-\frac{\varepsilon_1}{kT}\right) - g_1 \gamma_1^2 \left(\frac{\varepsilon_1^2}{(kT)^2} - \frac{\varepsilon_1}{kT} \right) \exp\left(-\frac{\varepsilon_1}{kT}\right)}{g_1 \exp\left(-\frac{\varepsilon_1}{kT}\right)} - \left[\frac{\left(g_1 \gamma_1 \frac{\varepsilon_1}{kT} \exp\left(-\frac{\varepsilon_1}{kT}\right) \right)^2}{g_1 \exp\left(-\frac{\varepsilon_1}{kT}\right)} \right] \right\}$$

$$\lim_{T \downarrow 0} K^{el} = \frac{nRT}{V} \left\{ \frac{g_1 \gamma_1 \frac{\varepsilon_1}{kT} - g_1 \gamma_1^2 \left(\frac{\varepsilon_1^2}{(kT)^2} - \frac{\varepsilon_1}{kT} \right)}{g_1} - \left[\frac{\left(g_1 \gamma_1 \frac{\varepsilon_1}{kT} \right)^2}{g_1} \right] \right\} = 0 \quad (14.36)$$

$$\lim_{T \downarrow 0} \left(\frac{\partial P^{el}}{\partial T} \right)_V = \frac{nR}{V} \left\{ \frac{g_1 \gamma_1 \frac{\varepsilon_1^2}{(kT)^2} \exp\left(-\frac{\varepsilon_1}{kT}\right)}{g_1 \exp\left(-\frac{\varepsilon_1}{kT}\right)} - \frac{g_1 \gamma_1 \frac{\varepsilon_1}{kT} \exp\left(-\frac{\varepsilon_1}{kT}\right) g_1 \frac{\varepsilon_1}{kT} \exp\left(-\frac{\varepsilon_1}{kT}\right)}{\left(g_1 \exp\left(-\frac{\varepsilon_1}{kT}\right) \right)^2} \right\} = 0 \quad (14.37)$$

14.3. Correction for 3rd law of entropy

From eqn. (14.32) follows that the entropy at zero temperature is only zero when the degeneracy of the ground state equals one. However, in the case of fayalite a description has been found by Aronson et al. (2007) in which the degeneracy of the ground state deviates from zero. When the third law is applicable, the partition function given by eqn. (14.2) must be used. This comes down to taking g_j/g_1 rather than g_j in all expressions for thermodynamic properties. Only entropy and Helmholtz energy are affected by that operation. In all other properties the substitution of g_j by g_j/g_1 results in cancelling-out the factor g_1 . By the substitution the expression for Helmholtz energy, corrected for the 3rd law, becomes:

$$A^{el} = -nRT \ln \left(\sum_{j=1}^m \frac{g_j}{g_1} e^{-x_j} \right) = nRT \ln(g_1) - nRT \ln \left(\sum_{j=1}^m g_j e^{-x_j} \right) = nRT \ln(g_1) - nRT \ln(Z_A) \quad (14.38)$$

$$\text{Using eqn. (14.6a), (14.31) and (14.38):} \quad \lim_{T \downarrow 0} A^{el} = 0 \quad (14.39)$$

For entropy eqn. (14.10) is corrected to:

$$S^{el} = nR \ln \left(\sum_{j=1}^m \frac{g_j}{g_1} e^{-x_j} \right) + nR \frac{\sum_{j=1}^m \frac{g_j}{g_1} x_j e^{-x_j}}{\sum_{j=1}^m \frac{g_j}{g_1} e^{-x_j}}, \quad \text{or:}$$

$$S^{el} = -nR \ln(g_1) + nR \ln \left(\sum_{j=1}^m g_j e^{-x_j} \right) + nR \frac{\sum_{j=1}^m g_j x_j e^{-x_j}}{\sum_{j=1}^m g_j e^{-x_j}} = -nR \ln(g_1) + nR \left\{ \ln(Z_A) + \frac{Z_S}{Z_A} \right\} \quad (14.40)$$

$$\text{Using eqn. (14.10), (14.32) and (14.40):} \quad \lim_{T \downarrow 0} S^{el} = 0 \quad (14.41)$$

Expressions for other properties, eqn.'s (14.19)-(14.23) remain unchanged.

14.4. Different octahedral sites

The expressions above were defined for one particular site. If more than one octahedral site is present such as for the fayalite and wadsleyite polymorphs of Fe_2SiO_4 , the Helmholtz energy is changed as follows. Assuming that equal amounts of octahedral sites are present in the crystal:

$$A^{elec} = \frac{1}{N_s} \left(\sum_{s=1}^{N_s} A_s^{el} \right) + A^{free,el} \quad (14.42)$$

Expression (14.42) describes the electronic contribution of a substance in which N_s sites are present, such as for the fayalite ($N_s=2$), wadsleyite ($N_s=3$) and ringwoodite ($N_s=1$) forms of Fe_2SiO_4 . The last term of eqn. (14.42) is a free electron gas contribution. It gives the possibility to represent heat capacity at high temperatures, such as possible for fayalite, or the Drude-like contribution to heat capacity for FeO as observed by Schrettle et al. (2012). Using eqn. (12.1) and (14.38), the Helmholtz energy is written as:

$$A^{elec} = -nRT \frac{1}{N_s} \sum_{s=1}^{N_s} \left(\ln \left(\sum_{j=1}^m \frac{g_{j,s}}{g_{1,s}} e^{-x_{j,s}} \right) \right) - \frac{1}{2} n \beta_{el} T^2 \left(\frac{V}{V_0} \right)^{\gamma_{el,free}} \quad (14.43)$$

In eqn. (14.43), V_0 represents the volume at zero temperature and zero pressure, and n is the number of atoms per formula unit ($n=2$ for fayalite) that may have crystal field splitting appearing in both terms on the right-hand side of eqn. (14.43).

14.5. Application to fayalite, Fe_2SiO_4

The Fe-atoms in Fe_2SiO_4 (fayalite) reside in two sites M1 and M2 of the crystal. When applying the formalism given in this section, the thermodynamic properties are calculated as follows. The properties calculated from the formalism are given per mole of formula unit Fe_2SiO_4 ($n=2$). Next we make the assumption that the number of M1 sites equals that of the M2 sites. Neglecting the free electron gas contribution, the electronic Helmholtz energy contribution is derived from eqn. (14.43) as:

$$\begin{aligned}
 A^{el} &= \frac{1}{2} (A^{el}(M1) + A^{el}(M2)) = \\
 A^{el} &= -\frac{1}{2} nRT \ln \left(\sum_{j=1}^{m_1} \frac{g_j}{g_1} e^{-x_j} \right) - \frac{1}{2} nRT \ln \left(\sum_{j=1}^{m_2} \frac{g_j}{g_1} e^{-x_j} \right) \\
 A^{el} &= \frac{1}{2} nRT \ln(g_1^{M1}) - \frac{1}{2} nRT \ln \left(\sum_{j=1}^{m_1} g_j e^{-x_j} \right) + \frac{1}{2} nRT \ln(g_1^{M2}) - \frac{1}{2} nRT \ln \left(\sum_{j=1}^{m_2} g_j e^{-x_j} \right) \quad (14.44)
 \end{aligned}$$

Burns (1978, 1985), Wood (1981) measured electronic transition energies for the t_{2g} and e_g levels in Fe_2SiO_4 . Aronson et al. (2007) showed by using neutron diffraction that spin-orbit coupling is present and that each level is split in five new levels with different energies. Combining their work with that of Burns (1985) the transitions are summarized in Table 14.1.

Aronson et al. (2007) showed that the shoulder in the heat capacity at 20 K results from the thermal population of the lower energy states in the crystal-field split manifold of the M1 site, located at 27 and 47 cm^{-1} above the ground state. These states explain the Schottky anomaly in the heat capacity curve below 20 K.

Table 14.1 Electronic transitions in fayalite Fe_2SiO_4 .

Nr	Energy/ cm^{-1}	assignment	degeneracy	site	reference
1	0	Ground state	1	M1	Aronson et al. (2007)
2	27	Spin-orbit	1	M1	Aronson et al. (2007)
3	47	Spin-orbit	1	M1	Aronson et al. (2007)
4	92	Spin-orbit	2	M1	Aronson et al. (2007)
5	730	δ_1	5	M1	Burns (1985)
6	1500	δ_2	5	M1	Burns (1985)
7	8060	e_g	5	M1	Burns (1985)
8	11060	e_g	5	M1	Burns (1985)
9	0	Ground state	1	M2	Aronson et al (2007)
10	8	Spin-orbit	3	M2	Aronson et al. (2007)
11	44	Spin-orbit	1	M2	Aronson et al. (2007)
12	1670	δ_1	5	M2	Burns (1985)
13	1670	δ_2	5	M2	Burns (1985)
14	8830	e_g	5	M2	Burns (1985)
15	9270	e_g	5	M2	Burns (1985)

The M2 site is responsible for the lambda transition at 65.8 K, the Neel temperature, associated with antiferromagnetic-ferromagnetic transition. The thermal population of the M2 manifold is governed by an exchange interaction and therefore the lambda transition is not represented by the formalism in section 14 alone. To describe the lambda transition due to the M2 site we used Inden's empirical formalism for magnetism presented in section 10 of this manual.

Additionally, to represent high temperature heat capacity data up to 400 K, Aronson et al. (2007) showed that it is necessary to assume that the ground state is 5-fold degenerate. That was achieved by merging the energy levels of the ground state and spin orbit of the M2 site (numbered 9, 10, and 11 in Table 14.1) into a new ground state for M2. To maintain the 3rd law for entropy, it is therefore necessary to start from eqn. (14.2) rather than from eqn. (14.1).

Aronson et al. (2007) determined the lambda shape in the heat capacity by determining the crystal field and vibrational contributions to heat capacity and their experimental data. This contribution is depicted in Figure 14.1 and we modelled it with Inden's (1981) formalism using 50 terms in the MacLaurin expression for isochoric heat capacity to achieve good convergence. However, assuming a magnetic moment $\beta=4$ bohr magneton (net spin $S=2$), Inden's formalism grossly overestimates the magnetic contribution to heat capacity. To arrive at an accurate description for the lambda contribution to heat capacity, a correction of their formalism must be applied, leading to a modification of eqn. (11.5) for the Helmholtz contribution:

$$A^\lambda = n_a \cdot g(\tau) \cdot m_f \cdot RT \ln(1 + \beta) \quad (14.45)$$

For fayalite m_f appears to be 0.3789.

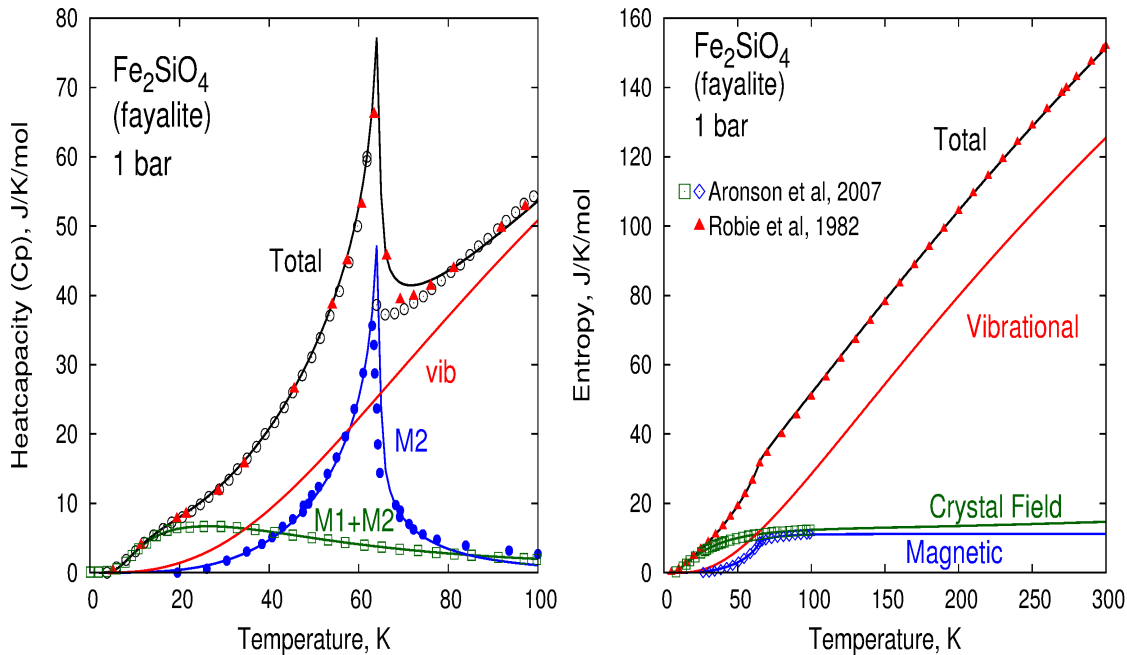


Fig. 14.1. Heat capacity and entropy calculated with *'me'* and input data of Table 14.2. Left: Experimental data are from: **total C_p** : Aronson et al. (2007, open black circle), Robie et al. (1982, solid red triangle); **Crystal-Field contribution**: Aronson et al. (2007, open green square); **Magnetic contribution**: Aronson et al. (2007, solid blue circle); **Vibrational contribution**: derived from the VDoS of Yu et al. (2013)

Table 14.2 below shows an input file for *'me'*. For the crystal-field electronic contribution we used the data in Table 14.1. These appear as coefficients in Table 14.2 on the blue lines. The lambda contribution appears as the green lines in Table 14.2.

14.6. Contributions to properties: programming

Vibrational, electronic and magnetic contributions to thermodynamic properties are not available in the output file of *'me'*; only the total properties are available. Contributions, such as depicted in

Figure 14.1, are calculated in procedure “`get_thermo_properties()`” of unit “`maketable.pas`”. To obtain values for the individual contributions, one could set one or more file(s) open in unit “`maketable.pas`” just before the call to procedure “`get_thermo_properties`”. Procedure “`get_thermo_properties`” is present in unit “`makevolume.pas`”. In that procedure, write temperature, pressure and thermodynamic properties values there and close the file(s) at the end of procedure “`maketable`” after the normal output table has been finished.

Table 14.2. Example of an input file for a 15-Einstein description

The following input data can be extracted from file [mgsifeo-15e-anh.mef](http://www.geo.uu.nl/~jacobs/Downloads), present on website <http://www.geo.uu.nl/~jacobs/Downloads>). The thermodynamic analysis is found in Jacobs et al (2019). The lines concerning magnetic and electronic contributions needed in the crystal field model are given in green and blue respectively. The contribution due to defects caused by vacancies is discussed in chapter 16.2.

```
<Fe2SiO4-oli>          (* Name of the substance *)
203.776000             (* Mass of the substance in gr/mol *)
7.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-1.55165070019255E+006 (* Static lattice energy in J/mol *)
4.59885769248535E-005 (* Volume/m3/mol at zero K and zero Pa *)
4.57327543493432E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
2                    (* l=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice
3                    (* Order of Birch-Murnaghan EoS of the static lattice *)
1.430858000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
5.000000000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero Pa *)
5.465837000000000E+010 (* Static lattice shear modulus/Pa at zero Pa *)
1.426500000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero Pa *)
1.000000000000000E+000 (* Vibrational parameter of the shear modulus *)
0                    (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
1                    (* 0=No magnetic contribution, 1=magnetic contribution *)
51                   (* Magnetic: number of terms in the Maclaurin series expansion >2 *)
2.800000000000000E-001 (* Magnetic: Ratio Energy(tau>1)/total Energy for magnetic transition
6.488000000000000E+001 (* Magnetic: Critical temperature Tc *)
4.000000000000000E+000 (* Magnetic: magnetic moment in Bohr magneton *)
3.000000000000000E+000 (* Magnetic: exponent (m) in Inden's (1981) expression for Cv below Tc
5.000000000000000E+000 (* Magnetic: exponent (n) in Inden's (1981) expression for Cv above Tc *)
2.000000000000000E+000 (* Magnetic: number of magnetic atoms per formula unit *)
3                    (* Crystal field electronic contribution *)
2                    (* Number of sites M1, M2, M3: maximum 3 sites *)
8                    (* Number of Crystal field energy levels of the M1 site *)
5                    (* Number of Crystal field energy levels of the M2 site *)
2.000000000000000E+000 (* Number of atoms per formula unit having crystal-field splitting *)
3.78868651539773E-001 (* Magnetic correction factor (mf): Helmholtz A=na.RT.g(t).mf.ln(1+b) *)
# Energy/cm^-1      Degeneracy Gruneisen parameter
# -----
0.000000E+000      1          0.000000E+000
2.700000E+001      1          0.000000E+000
4.700000E+001      1          0.000000E+000
9.200000E+001      2          0.000000E+000
7.300000E+002      5          0.000000E+000
1.500000E+003      5          0.000000E+000
8.060000E+003      5          0.000000E+000
1.106000E+004      5          0.000000E+000
0.000000E+000      5          0.000000E+000
1.670000E+003      5          0.000000E+000
1.670000E+003      5          0.000000E+000
8.830000E+003      5          0.000000E+000
9.270000E+003      5          0.000000E+000
# Extra Free electron gas contribution
# Cv(electronic)=Cv(crystal-Field)+a*T*(V/V0)^gamma_el
0.000000000000000E+000 (* Electronic Gruneisen parameter, gamma_el *)
0.000000000000000E+000 (* Electronic coefficient, a, in J/K/K/mol atoms that give crystal-field
0                    (* 0=No cation disorder, 1=cation disorder: model of O'Neill and Navrot
1                    (* 0= No monovacancy defects, 1=monovacancy defects *)
#                    (* Model: Dorogokupets & Oganov 2007 Phys Rev B 75:024115 *)
#                    (* Helmholtz energy = -(3/2)nRT*exp(s*eta^f-h*eta^g/T) *)
#                    (* with n=# atoms/formula unit, eta=V/V0 *)
8.167241300000000E+003 (* h: enthalpy of formation, K *)
0.000000000000000E+000 (* s: entropy, no unit *)
-1.000000000000000E+000 (* f *)
```

```

-5.000000000000000E-001      (* g *)
# Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
15                             (* Number of Einstein modes *)
2                               (* l=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by Stixru
# j   Theta/K      Fraction      Gamma      Mode_m(q)   Gamma_inf   a0          z
#-----
1    49.113946    7.514304284E-003  1.6967220  1.8464070  0.0000000  -2.930085E-005  0.0000000
2    147.341408   1.059256204E-001  1.6967220  1.8464070  0.0000000  -2.930085E-005  0.0000000
3    245.569013   1.419665680E-001  1.6967220  1.8464070  0.0000000  -2.930085E-005  0.0000000
4    343.796618   1.287064419E-001  1.6967220  1.8464070  0.0000000  -2.930085E-005  0.0000000
5    442.024223   1.418760128E-001  1.6967220  1.8464070  0.0000000  -2.930085E-005  0.0000000
6    540.251828   5.330142605E-002  0.9942005  1.8179560  0.0000000  -2.930085E-005  0.0000000
7    638.479433   1.112511380E-001  0.2916790  1.7895050  0.0000000  -2.930085E-005  0.0000000
8    736.707038   5.582992651E-002  0.2916790  1.7895050  0.0000000  -2.930085E-005  0.0000000
9    834.934643   3.999175335E-002  0.2916790  1.7895050  0.0000000  -2.930085E-005  0.0000000
10   933.162105    2.606744933E-005  0.2916790  1.7895050  0.0000000  -2.930085E-005  0.0000000
11  1031.389710    2.606744933E-005  0.2916790  1.7895050  0.0000000  -2.930085E-005  0.0000000
12  1129.617315    7.495166410E-002  0.2916790  1.7895050  0.0000000  -2.930085E-005  0.0000000
13  1227.844920    7.507431413E-002  0.2916790  1.7895050  0.0000000  -2.930085E-005  0.0000000
14  1326.072525    3.689459159E-002  0.2916790  1.7895050  0.0000000  -2.930085E-005  0.0000000
15  1424.300130    2.666410395E-002  0.2916790  1.7895050  0.0000000  -2.930085E-005  0.0000000
#
# sum of all fractions:  1.0000000000E+000
#####
# Isobaric calculation
1                               (* l=Isobaric calculation, 2=Isothermal calculation *)
0      400      2                (* Temperature range and step: T_start/K, T_end/K, T_step/K *)
1e+05 1e+05  0.0              (* Pressure range and step   : P_start/Pa, P_end/Pa, P_step/Pa *)
1                               (* Output: 1=Output to screen and file, 0=Output to file only *)
# Output file name
/home/michel/geodata/fayalite/fayalite.out
#####

```

Representing vibrational density of states with *'me'*

M.H.G. Jacobs, Institute of Metallurgy, TU-Clausthal, Germany, August 4th, 2016, last update April 5th, 2018

This part of the manual describes how to construct a plot of the vibrational density of states for a substance with *'me'*. Because thermodynamic analyses of substances are constrained by the VDoS derived from experiments or predicted from ab initio, an example is given how to construct a *'me'* input file from a VDoS.

15. Plotting a VDoS with 'me'

The input file, **demo.mef**, contains data that can be used in the multiple-Einstein program, 'me'. Program 'me' enables calculating a VDoS, which is plotted with open-software program 'GnuPlot'.

Example:

Calculate the VDoS of MgO at zero pressure and zero temperature. Use a 5-Einstein model.

To construct a table with thermodynamic properties we follow the 5 steps described below:

1. Select the description of MgO given in section 3, Table 3.1.
2. Copy the data from **demo.mef** and store them on a new file '**mgo.mef**'. File '**mgo.mef**' will look like:

```
# Comment: File mgo.mef with data copied from file demo.mef
#
<MgO-pc> (* Name of the substance *)
40.304000 (* Mass of the substance in gr/mol *)
2.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-6.21124727753588E+005 (* Static lattice energy in J/mol *)
1.12027710146365E-005 (* Volume/m3/mol at zero K and zero Pa *)
1.10725544416607E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
2 (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice *)
3 (* Order of Birch-Murnaghan EoS of the static lattice *)
1.713650000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
4.185889000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero *)
1.398012000000000E+011 (* Static lattice shear modulus/Pa at zero Pa *)
2.274201000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero *)
2.068608000000000E+000 (* Vibrational parameter of the shear modulus *)
0 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st ord *)
0 (* 0=No magnetic contribution, 1=magnetic contribution *)
0 (* No electronic contribution *)
0 (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984)*)
0 (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &...*)
# Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
5 (* Number of Einstein modes *)
2 (* 1=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by
Stixrude & Lithgow-Bertelloni, 2005 *)
# j Theta/K Fraction Gamma Mode_m(q) Gamma_inf a0 z
# -----
1 103.6373 8.906551151E-003 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
2 310.9115 1.518128083E-001 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
3 518.1859 4.489913319E-001 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
4 725.4603 3.115346305E-001 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
5 932.7346 7.875467817E-002 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
#
# sum of all fractions: 1.000000000E+000
#####
```

3. Next information must be attached to file '**mgo.mef**' specifying that a VDoS is calculated. Go to the last part of file '**demo.mef**' and copy the lines of 'example 2':

```
# VDoS calculation; this part must be attached
3 (* 1=Isobaric calculation, 2=Isothermal calculation, 3=VDoS *)
1 (* Desired unit: 1=cm^-1, 2=THz, 3=meV *)
0 0 (* Pressure/Pa, Temperature/K at which VDoS is calculated *)
# Script file for GnuPlot:
/home/michel/geodata/mgo/mgo.grf
1 (* 0=No experimental/abinitio VDoS, 1=experimental/abinitio VDoS *)
# When the preceding line defines an experimental/abinitio VDoS add the following 3 lines:
# File with experimental/abinitio VDoS (X,Y) points:
/home/michel/geodata/mgo/vdosmgo.exp
1 (* Unit experimental/abinitio VDoS: 1=cm^-1, 2=THz, 3=meV *)
# -----
```


We wish to calculate the VDoS expressing the frequencies in wave numbers with unit cm^{-1} . That is called the *'desired unit'* (3rd line). On the 4th line we specify the pressure and temperature at which the VDoS should be calculated. The frequencies in the VDoS are volume dependent; therefore the VDoS changes with pressure and temperature. On the 6th line a script file for *'GnuPlot'* is specified. If a VDoS is available from e.g. ab initio or from inelastic neutron scattering experiments, the flag on the 7th line can be set to '1' and the name of the file containing (X,Y) points specifying the VDoS should be entered on the 10th line. Take care that the correct path and file name is set. Also take care that the correct unit of the experimental or ab initio VDoS is entered on the 11th line. If no VDoS from experiments or ab initio is available, set the flag on the 7th line to '0' and comment-out or delete lines 10 and 11.

4. Insert these lines into file **'mgo.mef'**. The final resulting file **'mgo.mef'** will look like:

```
# Comment: File mgo.mef with data copied from file demo.mef: final result
#
<MgO-pc>          (* Name of the substance *)
 40.304000         (* Mass of the substance in gr/mol *)
2.0000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-6.21124727753588E+005 (* Static lattice energy in J/mol *)
1.12027710146365E-005 (* Volume/m3/mol at zero K and zero Pa *)
1.10725544416607E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
2                (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice
3                (* Order of Birch-Murnaghan EoS of the static lattice *)
1.7136500000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
4.1858890000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero
1.3980120000000000E+011 (* Static lattice shear modulus/Pa at zero Pa *)
2.2742010000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero
2.0686080000000000E+000 (* Vibrational parameter of the shear modulus *)
0                (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st ord
0                (* 0=No magnetic contribution, 1=magnetic contribution *)
0                (* No electronic contribution *)
0                (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984)*)
0                (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &...*)
# Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
5                (* Number of Einstein modes *)
2                (* 1=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by
Stixrude & Lithgow-Bertelloni, 2005 *)
# j   Theta/K   Fraction          Gamma      Mode_m(q)   Gamma_inf   a0          z
# -----
1   103.6373   8.906551151E-003   1.5153760   1.3987510   0.0000000   9.108297E-006   7.2990600
2   310.9115   1.518128083E-001   1.5153760   1.3987510   0.0000000   9.108297E-006   7.2990600
3   518.1859   4.489913319E-001   1.5153760   1.3987510   0.0000000   9.108297E-006   7.2990600
4   725.4603   3.115346305E-001   1.5153760   1.3987510   0.0000000   9.108297E-006   7.2990600
5   932.7346   7.875467817E-002   1.5153760   1.3987510   0.0000000   9.108297E-006   7.2990600
#
# sum of all fractions: 1.000000000E+000
#####
# VDoS calculation; this part is now attached
3                (* 1=Isobaric calculation, 2=Isothermal calculation, 3=VDoS *)
1                (* Desired unit: 1=cm^-1, 2=THz, 3=meV *)
0 0              (* Pressure/Pa, Temperature/K at which VDoS is calculated *)
# Script file for GnuPlot:
/home/michel/geodata/mgo/mgo.grf
1                (* 0=No experimental/abinitio VDoS, 1=experimental/abinitio VDoS *)
# When the preceding line defines an experimental/abinitio VDoS add the following 3 lines:
# File with experimental/abinitio VDoS (X,Y) points:
/home/michel/geodata/mgo/vdosmgo.exp
1                (* Unit experimental/abinitio VDoS: 1=cm^-1, 2=THz, 3=meV *)
# -----
```

5. The VDoS is constructed by calling the multiple-Einstein program *'me'* with the input file as argument.

- Open a terminal in Ubuntu by pressing simultaneously: cntrl-alt-t (Alternatively in Windows open powershell or command prompt)
- Go to the directory where program *'me'* is present
- When file **'mgo.mef'** is present in the same directory as program *'me'* type:

- ```
./me mgo.mef
```
- (alternatively in powershell, command prompt of windows: `.\me mgo.mef`)
- The output file **mgo.grf** is created in the desired directory.
  - A plot is made by typing in the directory where **mgo.grf** is present: `gnuplot mgo.grf` -

The top-left frame of Figure 15.1 shows the result. Jacobs et al. (2017) performed a thermodynamic analysis of the system MgO-SiO<sub>2</sub>. The right-hand frame of Figure 15.1 shows that when the same operations are carried out for a 60-Einstein model for MgO, present in file **mgosio2-60e.mef**, the resulting VDoS resembles better that predicted by Wu et al. (2009).

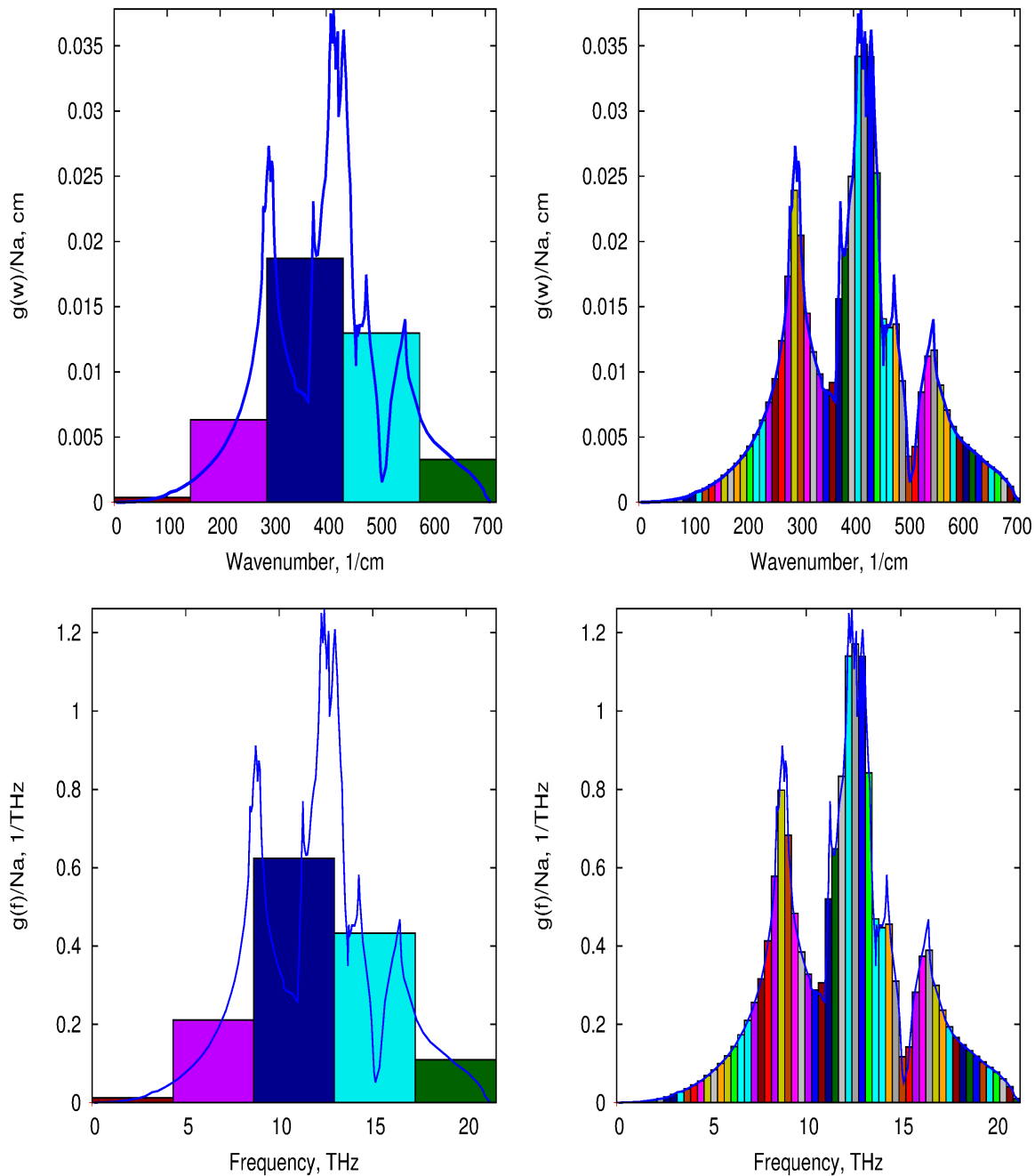


Fig. 15.1. VDoS of MgO calculated by *'me'*. Left frames using 5 Einstein frequencies in the VDoS. Right frames using 60 Einstein frequencies in the VDoS. The solid blue curve has been predicted by Wu et al. (2009). Bottom two frames: the *'desired unit'* for frequency has been taken as THz instead of cm<sup>-1</sup>. *Na* represents Avogadro's number

Note that an experimentally established or ab initio predicted VDoS, read-off from plots published in the literature, often has arbitrary units on the  $Y$ -axis. *'me'* corrects automatically for that because the surface underneath the  $g(w)$  curve is always a constant,  $3nN_A$ , and the surface underneath  $g(w)/N_A$  is  $3n$ , with  $n$  the number of atoms in one mole of molecular formula unit.

In the thermodynamic analysis of MgO, Jacobs et al. (2017) started with the VDoS of Wu et al. (2009) and partitioned it in 60 Einstein continua as depicted on the right-hand frames of Figure 15.1. The frequency width of each continuum was determined by the largest frequency of the VDoS, about  $700 \text{ cm}^{-1}$  and the number of Einstein frequencies. Their next step was to set one Einstein frequency in the middle of each continuum, resulting in the frequency (Einstein temperature) part of the input data file for *'me'*. In the construction of the VDoS above, the reverse route is followed from Einstein monochromatic frequencies to Einstein continua.

### 15.1. Constructing a *'me'* input file for MgO from an ab initio VDoS

Jacobs et al. (2017) showed that the VDoS predicted by ab initio puts tight constraints on the thermodynamic analysis of substances in the system MgO-SiO<sub>2</sub>. The first step in such an analysis is the construction of an input file that represents the VDoS in terms of frequencies and their fractions. To achieve that we use a separate program, *'medos'*, that constructs a file which serves as input for program *'me'*. Program *'medos'* uses of a script file in the same way as *'me'*. An example is given below and is obtained by copying example 3 from the last part of file [demo.mef](#).

```

Example 3: making a VDoS from experimental/abinitio VDoS (program 'medos')

60 (* Desired number of Einstein temperatures *)
Output file serving as input file for 'me'
/home/michel/geodata/mgo/mgo60.mef
1 (* VDoS unit: 1=cm^-1, 2=THz, 3=meV *)
File containing experimental/abinitio VDoS (X,Y) points
/home/michel/geodata/mgo/vdosmgo.exp

```

The script file starts with specifying the desired number of Einstein temperatures in the VDoS on the 4<sup>th</sup> line and an output file on the 6<sup>th</sup> line. The output file serves as input file for *'me'*. The 7<sup>th</sup> line specifies the frequency unit that is used in the VDoS that is available from experiments or ab initio predictions. That is important because these frequencies must be converted to Einstein temperatures. Conversion takes place in *'medos'* according to eqn. 15.1.

$$\theta_j = \frac{h \times 10^{12} \nu_j / \text{THz}}{k} = \frac{hc \times 10^2 w_j / \text{cm}^{-1}}{k} = \frac{q_e \times 10^{-3} E_j / \text{meV}}{k} \quad (15.1)$$

In eqn. (15.1),  $h$  denotes Planck's constant,  $k$  Boltzmann's constant,  $c$  the velocity of light in vacuum and  $q_e$  the elementary charge.

The name of the file containing frequencies and the VDoS value is given on the 9<sup>th</sup> line of the script file above. In many cases, especially when a VDoS is read from a plot in a journal paper, the VDoS value is expressed in an arbitrary unit. The surface underneath the VDoS represents the degrees of vibrational freedom,  $3nN_A$ . Program *'medos'* uses the VDoS values to establish the fractions in the expressions for vibrational contributions to thermodynamic properties, such as in eqn. (6.3) of section 6. That is achieved by calculating the surface underneath the experimental or ab initio VDoS, requiring a sufficient number of points to achieve sufficient accuracy. In the case of

'**vdosmgo.exp**' in the script file above we used about 160 points. In cases that a VDoS is read-off from a plot this is an important step.

The algorithm used by '**medos**' is kept very simple by connecting the (X,Y) points with lines. By setting the desired number of frequencies to 60, the VDoS is sliced in 60 continua (boxes), resulting in an Einstein continuum model similar to Kieffer's (1979) model. Because the highest frequency in '**vdosmgo.exp**' is  $710 \text{ cm}^{-1}$ , each continuum has a width of about  $12 \text{ cm}^{-1}$ . The height of each continuum is determined via an interpolation process. Therefore a sufficient number of points is important. '**medos**' uses a simple smoothing technique by averaging 20 VDoS values in each of the 60 continua.

Program '**medos**' is a FreePascal program, which is compiled by:

```
fpc medos.pas
```

The input file **mgo60.mef** for '**me**' is constructed by using the name of the script file as argument. For example by typing at the command prompt:

```
./medos makevdos.mgo (in Linux) or .\medos makevdos.mgo (in Windows powershell)
```

Because model parameters, such as equation of state properties, or Grüneisen and anharmonicity parameters are unknown to '**medos**' it uses preset values for static properties in the construction of the output file, namely those for MgO determined by Jacobs et al. (2017). Note that Einstein temperatures appearing in the resulting output file, **mgo60.mef**, are valid at zero temperature and zero pressure. Because static and vibrational model parameters are unknown a priori, '**medos**' assumes that the frequencies in '**vdosmgo.exp**' are valid at this condition. That is the case for many ab initio predictions, but exceptions are possible, such as for instance for post-perovskite and the high pressure form of clinoenstatite, both not stable at 1 bar pressure. In these cases the resulting Einstein temperatures must be considered approximations, which must be fine-tuned later in a thermodynamic analysis using an optimizer.

The resulting file **mgo60.mef** can be used as input for '**me**' by proceeding in the same way as in the preceding section by attaching 'example 2' in last part of file **demo.mef**, see below.

**3.** Next information must be attached to file '**mgo60.mef**' specifying that a VDoS is calculated.

Go to the last part of file '**demo.mef**' and copy the lines of 'example 2'. Change pressure and temperature, and select the name of the GnuPlot file and location of the VDoS file:

```
VDoS calculation; this part must be attached
3 (* 1=Isobaric calculation, 2=Isothermal calculation, 3=VDoS *)
1 (* Desired unit: 1=cm^-1, 2=THz, 3=meV *)
0 0 (* Pressure/Pa, Temperature/K at which VDoS is calculated *)
Script file for GnuPlot:
/home/michel/geodata/mgo/mgo60.grf
1 (* 0=No experimental/abinitio VDoS, 1=experimental/abinitio VDoS *)
When the preceding line defines an experimental/abinitio VDoS add the following 3 lines:
File with experimental/abinitio VDoS (X,Y) points:
/home/michel/geodata/mgo/vdosmgo.exp
1 (* Unit experimental/abinitio VDoS: 1=cm^-1, 2=THz, 3=meV *)

```

When using the new **mgo60.mef** in '**me**' by typing at the command prompt:

```
./me demo60.mef (in Linux) or .\me demo60.mef (in Windows powershell)
```

, plots are obtained as shown on the right-hand side frames of Figure 15.1.

It is of course not surprising that the resulting VDoS quite accurately represents that obtained from ab initio because the preset values taken in *'medos'* resemble those from a thermodynamic analysis for MgO. Therefore we repeat the procedure for Mg<sub>2</sub>SiO<sub>4</sub>, ringwoodite, in section 15.2 to show that at least reasonable heat capacities can be established when we do not have correct preset values.

### 15.2 Constructing a *'me'* input file for Mg<sub>2</sub>SiO<sub>4</sub> (ringwoodite) from an abinitio VDoS

Ringwoodite is a high pressure form of forsterite, and it can be quenched to 1 bar pressure. We start with the VDoS predicted by Yu and Wentzcovitch (2006). The VDoS is given in file **vdos-ri.exp**. We apply program *'medos'* with the script file below.

```
Script file for 'medos' to make an input file for 'me'
60 (* Desired number of Einstein temperatures *)
Output file serving as input file for 'me'
/home/michel/geodata/ringwoodite/mg-ri.mef
1 (* VDoS unit: 1=cm^-1, 2=THz, 3=meV *)
File containing VDoS (X,Y) points
/home/michel/geodata/ringwoodite/vdos-ri.exp
```

First select the path of the output file and the file containing the VDoS points. Next give the script file a name, e.g. makevdos.ri, and type at the command prompt:

`./medos makevdos.ri` (Linux) or `.\medos makevdos.ri` (Windows powershell)

*'medos'* produces the output file **mg-ri.mef** and a part of it is given below.

```
=====
Note that values have been preset to those for MgO !!
Only Theta and Fractions were determined with program 'mevdos'...
=====
#
MgO (Preset...) (* Name of the substance *)
40.304 (* Mass of the substance in gr/mol *)
7.00 (* Number of atoms in 1 molecular formula unit *)
-6.21093534291483E+005 (* Static lattice energy in J/mol *)
1.12027710146365E-005 (* Volume/m3/mol at zero K and zero Pa *)
1.10736889124136E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
2 (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice *)
3 (* Order of Birch-Murnaghan EoS of the static lattice *)
1.71365000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
4.18588900000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero Pa *)
1.39801200000000E+011 (* Static lattice shear modulus/Pa at zero Pa *)
2.27420200000000E+000 (* Pressure derivative of the static lattice shear modulus at zero Pa *)
2.06860800000000E+000 (* Vibrational parameter of the shear modulus *)
0 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
0 (* 0=No magnetic contribution, 1=magnetic contribution *)
0 (* No electronic contribution *)
0 (* 0=No cation disorder, 1=model of O'Neill and Navrotsky (1983,1984) *)
0 (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &... *)
60 (* Number of Einstein modes *)
2 (* 1=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by
Stixrude & Lithgow-Bertelloni, 2005 *)
j Theta/K Fraction Gamma Mode_m(q) Gamma_inf a0 z

1 11.736120 5.40560570E-0005 1.0000000 0.1000000 0.0000000 1.00000E-0011 0.0000000
2 35.207929 1.67858282E-0004 1.0000000 0.1000000 0.0000000 1.00000E-0011 0.0000000
.
.
. etc
```

Now we deliberately make a mistake, namely that we do not change the model parameters. Static model parameters are than the same as for MgO. Because the molar volume of ringwoodite is about 39.4 cm<sup>3</sup>/mol, our volume 11.2 cm<sup>3</sup>/mol would than be about 3-4 times too small. According to Jacobs et al. (2017) the static bulk modulus of ringwoodite is about 192 GPa, which is considerably larger than in **mg-ri.mef**. We have only changed the number of atoms in one molecular formula

unit because we know that there are 7 atoms in  $\text{Mg}_2\text{SiO}_4$  instead of 2 in  $\text{MgO}$ . We also keep the preset values for Grüneisen and mode- $q$  parameters unchanged.

Now we calculate the VDoS and additionally the heat capacity with *'me'*, by attaching subsequently the parts of example 1 and example 2, present at the end of file `demo.mef`, to `mg-ri.mef`. Figure 15.2 shows that the results are surprisingly good up to room temperature. Why does this work so well?

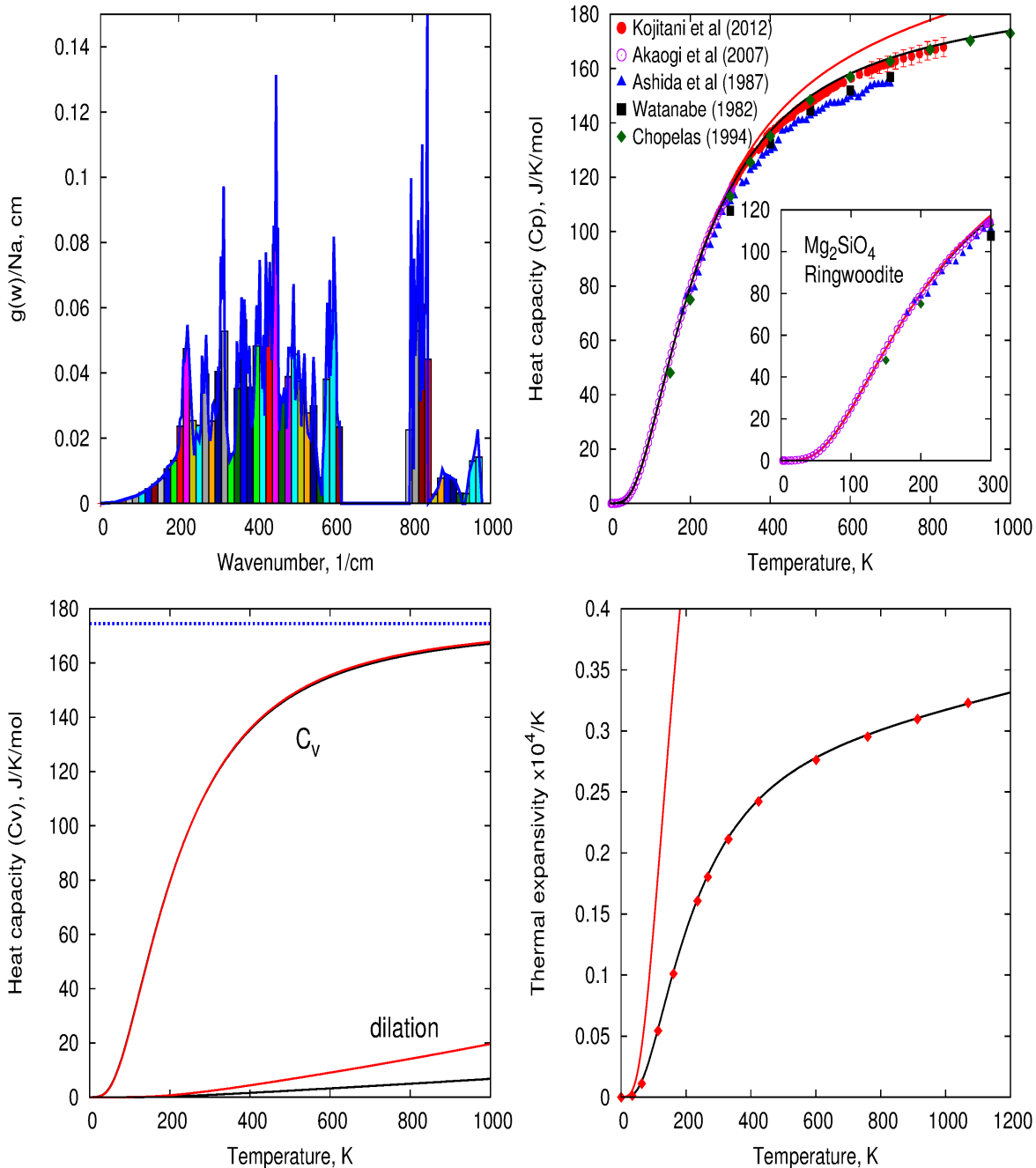


Fig 15.2. **Top-left:** VDoS of ringwoodite calculated by *'medos'* as the coloured boxes compared with the ab initio prediction of Yu & Wentzcovitch (2006). **Top-right:** isobaric heat capacity calculated by *'me'* as the red curve and that calculated by Jacobs et al (2017) as the black curve. **Bottom-left:** isochoric heat capacity and dilation term; red curves calculated with *'me'* using `mg-ri.mef`, black curves by Jacobs et al (2017). **Bottom-right:** thermal expansivity calculated by *'me'* (red) and Jacobs et al (2017, black), data points predicted by Wu & Wentzcovitch (2006)

When we start making the VDoS, *'medos'* assumes that the frequencies in the VDoS of Yu and Wentzcovitch (2006) were given at zero temperature and zero pressure, which is indeed the case. Subsequently, *'me'* calculates the VDoS as zero temperature and zero pressure. That requires the calculation of the volume at zero temperature and zero pressure. That results in the volume,  $V_0$ . Inserting  $V_0$  in eqn. (6.10) and (6.9) of section 6 results in the frequencies at zero temperature and zero pressure, i.e. the input frequencies of [mg-ri.mef](#). Although the calculated volume  $V_0$ , is about 3-4 times to small, the correct frequencies are found back at zero temperature and zero pressure and therefore the VDoS as well.

The isobaric heat capacity,  $C_p$ , is calculated from the isochoric heat capacity,  $C_v$ , and the dilation term according to:

$$C_p = C_v + \alpha^2 KVT \quad (15.2)$$

The bottom-left frame of Figure 15.2 shows that the difference between  $C_v$  calculated by *'me'* and that of Jacobs et al. (2017) is quite small. Because the ratio  $V/V_0$  does not change significantly at low temperature, vibrational frequencies, which depend on the ratio  $V/V_0$ , are not significantly different for both methods. The  $x_j$  in the expression for  $C_v$ , eqn. (6.24a), are than mainly dependent on temperature via eqn. (6.1), and much less on the change in frequencies with the volume ratio.

The bottom-right frame shows that thermal expansivity calculated with [mg-ri.mef](#) is about 3-4 times larger than that calculated by Jacobs et al. (2017). That this is the case becomes clear by rewriting eqn. (6.26a) as:

$$\left( \frac{\partial P^{vib}}{\partial T} \right)_V = \frac{\gamma C_v}{V} \quad (15.3)$$

To arrive at (15.3) we made use of eqn. (6.24a) and by neglecting anharmonicity, as is the case here, and by setting all Grüneisen parameters to the same value,  $\gamma$ . The value of  $\gamma$  in [mg-ri.mef](#) is 0.8 times that used in Jacobs et al. (2017). Because volume calculated with [mg-ri.mef](#) is about 3-4 times smaller, the isochoric temperature derivative of thermal pressure is about 3-4 times larger. Because thermal expansivity is related to this property, via eqn. (15.4), that also holds for thermal expansivity.

$$\alpha = \frac{1}{K} \left( \frac{\partial P^{vib}}{\partial T} \right)_V \quad (15.4)$$

Although thermal expansivity resulting from our *'me'* calculation is much larger than that of Jacobs et al. (2017), the dilation term,  $\alpha^2 KVT$ , depicted in the bottom-left frame of Figure 15.2 is small at low temperatures. Because of that characteristic the difference between isochoric and isobaric heat capacity is quite small at low temperature, being zero at zero temperature. Because the VDoS is the same for both methods, also  $C_v$  and  $C_p$ , are insignificantly different at low temperature. The difference in isobaric heat capacity of the two methods becomes significant when the difference in the dilation terms becomes larger, in this case above room temperature.

### Conclusion

Although volume and bulk modulus in the input file differ considerably from experimental values, quite accurate values for low-temperature heat capacity can be obtained. Low-temperature heat

capacity mainly depends on the form of the VDoS. If static parameters in file **mg-ri.mef** would be replaced by eg experimental values at ambient conditions, deviations would be much smaller and quite accurate heat capacity up to high temperatures can be obtained, even without using an optimizer.

### 15.3 Changing model parameters manually

When model parameters in the input file of **'me'** are changed manually, some messages may appear in the output file. This also occurs when an input file prepared by **'medos'** is used by **'me'**. An example is given below when an input file for **'me'** is constructed from an abinitio VDoS for MgO with **'medos'**. When the input file is used in **'me'** the following message is displayed in the **'GnuPlot'** file:

```

This file calculated by: me (Version 6: April 5th, 2018)
Input file : /home/michel/geodata/mgo/mgo60.mef
Constructed on: May 6th, 2018 / 14hr:50min:45sec
#
Script file for Gnuplot: Vibrational Density of States
The resulting VDoS values are g(w)/Na in 1/cm-1, where g(w) is the
wavenumber VDoS, and w in cm-1. Na is Avogadros number.
Experiments: /home/michel/programs/short/vdosmgo.exp
See end of this file for conversion to *.eps file for use in GIMP
#
Pressure = 0.000000E+0000 Pa
Temperature = 0.000000E+0000 K
Volume = 1.120277E+0001 cm3/mol
#
#####
Model parameters were changed or preset in the input file. Therefore the total
equation of state pressure, P_total(T=0,V0), does not match the external
pressure at (0 K, 0 Pa).
'me' repaired this by changing the static volume. The model parameters now give
P_total(T=0,V0) = 0 when the external pressure is zero.
#
Old static volume: 11.073689 cm3/mol
New static volume: 11.118020 cm3/mol
Difference : 0.044331 cm3/mol [0.400328%]
#####

#
Set terminal to wxt: comment this line when plotting to file with extension .eps
set terminal wxt
```

Blue lines indicate that static volume required a correction. Such message is also displayed when the input file for **'me'** is used to make a table such as indicated below.

```
This file calculated by: me (Version 6: April 5th, 2018)
Input file: /home/michel/geodata/mgo/mgo60-1.mef
Constructed on : May 6th, 2018 / 14hr:50min:53sec
Isobaric calculation
Substance name: MgO
Pressure starts at: 100.0000 KPa
#####
Model parameters were changed or preset in the input file. Therefore the total
equation of state pressure, P_total(T=0,V0), does not match the external
pressure at (0 K, 0 Pa).
'me' repaired this by changing the static volume. The input parameters now give
P_total(T=0,V0) = 0 when the external pressure is zero.
#
Old static volume: 11.073689 cm3/mol
New static volume: 11.118020 cm3/mol
Difference : 0.044331 cm3/mol [0.400328%]
#####
T/K P/KPa V/cm3/mol d/gr/cm3 a*1E+4/K K/GPa Cp/J/K/mol Cv/J/K/mol Ks

```



When **'me'** calculates thermodynamic properties at a specific condition of pressure and temperature, it starts with calculating the volume from the pressure equation. We illustrate this for a simple case, using a Vinet equation of state for the static lattice and by assuming that the substance is described by a single Einstein frequency in the quasi-harmonic approximation. By using eqn. (6.25a) we have:

$$P = 3K_0^{st} \left[ \left( \frac{V}{V_0^{st}} \right)^{-2/3} - \left( \frac{V}{V_0^{st}} \right)^{-1/3} \right] \exp \left\{ \frac{3}{2} (K_0^{st} - 1) \left[ 1 - \left( \frac{V}{V_0^{st}} \right)^{1/3} \right] \right\} + \frac{3nRT\gamma}{V} \left\{ \frac{x}{2} + \frac{x}{e^x - 1} \right\} \quad (15.5)$$

$$x = \frac{h\nu}{kT} = \frac{\theta}{T}$$

The frequency,  $\nu$ , and Grüneisen parameter  $\gamma$  depend on volume. At zero pressure and zero temperature, eqn. (15.5) is written to:

$$0 = 3K_0^{st} \left[ \left( \frac{V_0}{V_0^{st}} \right)^{-2/3} - \left( \frac{V_0}{V_0^{st}} \right)^{-1/3} \right] \exp \left\{ \frac{3}{2} (K_0^{st} - 1) \left[ 1 - \left( \frac{V_0}{V_0^{st}} \right)^{1/3} \right] \right\} + \frac{3nR\gamma_0}{V_0} \frac{\theta_0}{2} \quad (15.6)$$

Eqn. (15.6) shows that model parameters cannot be changed independently, but that one parameter can be expressed in the others. For the substances in file **demo.mef** the parameters were optimized such way that eqn. (15.6) holds.

When a model parameter is changed, or in the case that an input file for **'me'** is prepared using **'medos'** and preset values are written in it, eqn. (15.6) does not hold anymore. For that reason **'me'** checks if eqn. (15.6) holds true before any calculations are carried out. Although any parameter can be selected to repair the condition of eqn. (15.6), **'me'** prefers to change the static volume  $V_0^{st}$ . That occurs in an iterative process. After that **'me'** continues making an output file.

Electronic, magnetic and crystal field parameters have no effect on eqn. (15.6) as long as these effects are volume independent. In that case their pressure contribution to the pressure is zero. Intrinsic anharmonicity affects eqn. (15.6). When anharmonicity is included in the pressure equation, eqn. (15.6) is extended using eqn. (6.25d), (6.18) and (6.19):

$$0 = 3K_0^{st} \left[ \left( \frac{V_0}{V_0^{st}} \right)^{-2/3} - \left( \frac{V_0}{V_0^{st}} \right)^{-1/3} \right] \exp \left\{ \frac{3}{2} (K_0^{st} - 1) \left[ 1 - \left( \frac{V_0}{V_0^{st}} \right)^{1/3} \right] \right\} + \frac{3nR\gamma_0}{V_0} \frac{\theta_0}{2} + \frac{3nR\theta^2 a_0}{12V_0} \left\{ \gamma_0 - \frac{z_0}{2} \right\} \quad (15.7)$$

Generally, when arbitrary numbers of Einstein temperatures are used in the VDoS, corrections of static volume are carried out when one or more parameters in the set  $V_0$ ,  $K_0^{st}$ ,  $K_0'^{st}$ ,  $\theta_{j,0}$ ,  $\gamma_{j,0}$ ,  $a_{j,0}$ ,  $z_{j,0}$  are changed.

# **Defect contributions**

M.H.G. Jacobs, Institute of Metallurgy, TU-Clausthal, Germany, April 5<sup>th</sup>, 2018

This part of the manual describes defect contributions to the Helmholtz energy: cation disorder and mono vacancies.

## 16.1 Cation disorder

Cation distribution in a large number of minerals, mostly spinels, has been extensively studied by Navrotsky and Kleppa (1967), Navrotsky (1977), and O'Neill and Navrotsky (1983,1984). The thermodynamic model describing the disorder of the cations in a crystal is described in these papers and in the book of Navrotsky (1994). It is based on an ion exchange reaction indicating that ions may interchange tetrahedral and octahedral sites. Applying the model to silicate spinels with the molecular formula  $M_2SiO_4$  one may write:



The metal ions, M, normally occupy the octahedral sites and the silicon atoms the tetrahedral sites. The general thermodynamic model is based on a two-sub lattice model in which the crystal lattice is partitioned in  $N^{tet}$  moles of tetrahedral and  $N^{oct}$  moles of octahedral sites per one mole of molecular formula unit. The site fractions,  $y$ , on these sub lattices are derived from the three relations:

$$y_M^{tet} + y_{Si}^{tet} = 1 \quad (16.2)$$

$$y_M^{oct} + y_{Si}^{oct} = 1 \quad (16.3)$$

$$n_{Si}^{oct} = n_M^{tet} \quad (16.4)$$

Relation (16.4) is due to the characteristic that the movement of one Si atom from a tetrahedral site to an octahedral site, is accompanied by the movement of M atom from an octahedral site to a tetrahedral site;  $n_{Si}^{oct}$  and  $n_M^{tet}$  denote the number of moles of Si atoms on octahedral sites and M atoms on tetrahedral sites per molecular formula unit. These numbers are related to site fractions by  $n_{Si}^{oct} = y_{Si}^{oct} N^{oct}$  and  $n_M^{tet} = y_M^{tet} N^{tet}$ . The thermodynamic model is written in terms of one independent site fraction,  $y_M^{tet}$ , by using relations (16.2)-(16.4) as:

$$y_M^{oct} = 1 - \frac{1}{L} y_M^{tet} \quad y_{Si}^{oct} = \frac{1}{L} y_M^{tet} \quad y_{Si}^{tet} = 1 - y_M^{tet} \quad L = \frac{N^{oct}}{N^{tet}} \quad (16.5)$$

The enthalpy of disorder is written as:

$$\Delta H^{dis} = \Delta U^{dis} + P\Delta V^{dis} \approx \Delta U^{dis} \quad (16.6)$$

O'Neill and Navrotsky (1983) demonstrated that  $\Delta V^{dis}$  is small enough to be neglected at low and moderate pressures. Using the formalism it has been shown that the enthalpy of disorder can be derived and rearranged as:

$$\Delta H^{dis} = H(y_M^{tet}) - H(y_M^{tet} = 0) = (\alpha_H + \beta_H y_M^{tet}) y_M^{tet} \quad (16.7)$$

In eqn. (16.7), the interchange enthalpy is defined as the change of enthalpy when reaction (16.1) is complete ( $y_M^{tet} = 1$ ):

$$\Delta H^{int} = \alpha_H + \beta_H \cdot y_M^{tet} \quad (16.8)$$

The configurational entropy is derived from:

$$\Delta S^{dis} = S(y_M^{tet}) - S(y_M^{tet} = 0) \quad (16.9)$$

$$S = -R \left( n_M^{tet} \ln n_M^{tet} + n_{Si}^{tet} \ln n_{Si}^{tet} \right) - R \left( n_M^{oct} \ln n_M^{oct} + n_{Si}^{oct} \ln n_{Si}^{oct} \right) \quad (16.10)$$

After rearrangement:

$$\Delta S^{dis} = -RN^{tet} \left( y_M^{tet} \ln y_M^{tet} + y_{Si}^{tet} \ln y_{Si}^{tet} \right) - RN^{oct} \left( y_M^{oct} \ln y_M^{oct} + y_{Si}^{oct} \ln y_{Si}^{oct} \right) \quad (16.11)$$

Inserting eqn. (16.5) gives:

$$\Delta S^{dis} = -R \left\{ N^{tet} \left[ \left( 1 - y_M^{tet} \right) \ln \left( 1 - y_M^{tet} \right) + y_M^{tet} \ln y_M^{tet} \right] + N^{oct} \left[ \frac{1}{L} y_M^{tet} \ln \left( \frac{1}{L} y_M^{tet} \right) + \left( 1 - \frac{1}{L} y_M^{tet} \right) \ln \left( 1 - \frac{1}{L} y_M^{tet} \right) \right] \right\} + \left( \alpha_S + \beta_S y_M^{tet} \right) y_M^{tet} \quad (16.12)$$

In eqn. (16.12) a non-configurational entropy has been added to the configurational entropy in the same way as for enthalpy.

The Gibbs energy of disorder is then expressed as:

$$\Delta G^{dis} = \left\{ \alpha_H + \beta_H y_M^{tet} \right\} y_M^{tet} + RT \left\{ N^{tet} \left[ \left( 1 - y_M^{tet} \right) \ln \left( 1 - y_M^{tet} \right) + y_M^{tet} \ln y_M^{tet} \right] + N^{oct} \left[ \frac{1}{L} y_M^{tet} \ln \left( \frac{1}{L} y_M^{tet} \right) + \left( 1 - \frac{1}{L} y_M^{tet} \right) \ln \left( 1 - \frac{1}{L} y_M^{tet} \right) \right] \right\} - T \left( \alpha_S + \beta_S y_M^{tet} \right) y_M^{tet} \quad (16.13)$$

The equilibrium value for site fraction  $y_M^{tet}$  is numerically evaluated from:

$$\left( \frac{\partial \Delta G^{dis}}{\partial y_M^{tet}} \right)_{P,T} = 0 \quad (16.14)$$

$$0 = \alpha_H + 2\beta_H y_M^{tet} + pRT \ln \frac{\left( y_M^{tet} \right)^2}{\left( 1 - y_M^{tet} \right) \left( L - y_M^{tet} \right)} - T \left( \alpha_S + 2\beta_S y_M^{tet} \right) \quad (16.15)$$

The change in isobaric heat capacity due to disorder is derived from the enthalpy change as:

$$\Delta C_p^{dis} = \left( \frac{\partial \Delta H^{dis}}{\partial T} \right)_P = \left( \alpha_H + 2\beta_H y_M^{tet} \right) \left( \frac{\partial y_M^{tet}}{\partial T} \right)_P \quad (16.16)$$

The change of site fraction with temperature is derived from (16.15) as:

$$\left( \frac{\partial y_M^{tet}}{\partial T} \right)_P = \left( \alpha_H + 2\beta_H y_M^{tet} \right) \left[ 2\beta_H T - 2\beta_S T^2 + pRT^2 \frac{2L - y_M^{tet} (1+L)}{y_M^{tet} (1 - y_M^{tet}) (L - y_M^{tet})} \right]^{-1} \quad (16.17)$$

### Example

An example for the format of the input file for the ringwoodite form of  $\text{Fe}_2\text{SiO}_4$  is given in Table 16.1, and was determined in Jacobs et al (2019). Lines in blue denote the part dealing with cation disorder.

**Table 16.1.** Part of an input file for the ringwoodite form of Fe<sub>2</sub>SiO<sub>4</sub>. The thermodynamic analysis can be found in Jacobs et al (2019) and the description below is extracted from [mgsifeo-60e-anh.sag](http://www.geo.uu.nl/~jacobs/Downloads) on website <http://www.geo.uu.nl/~jacobs/Downloads>.

```

<Fe2SiO4-rin> (* Name of the substance *)
203.776000 (* Mass of the substance in gr/mol *)
7.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-1.54384774401370E+006 (* Static lattice energy in J/mol *)
4.19350240100317E-005 (* Volume/m3/mol at zero K and zero Pa *)
4.16559247148284E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
2 (* 1=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice
3 (* Order of Birch-Murnaghan EoS of the static lattice *)
2.131513000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
4.326920000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero Pa *)
1.027799000000000E+011 (* Static lattice shear modulus/Pa at zero Pa *)
1.388334000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero Pa *)
2.521925000000000E+000 (* Vibrational parameter of the shear modulus *)
0 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
1 (* 0=No magnetic contribution, 1=magnetic contribution *)
51 (* Magnetic: number of terms in the MacLaurin series expansion >2 *)
2.800000000000000E-001 (* Magnetic: Ratio Energy(tau>1)/total Energy for magnetic transition
1.183000000000000E+001 (* Magnetic: Critical temperature Tc *)
4.000000000000000E+000 (* Magnetic: magnetic moment in Bohr magneton *)
3.000000000000000E+000 (* Magnetic: exponent (m) in Inden's (1981) expression for Cv below Tc
5.000000000000000E+000 (* Magnetic: exponent (n) in Inden's (1981) expression for Cv above Tc
2.000000000000000E+000 (* Magnetic: number of magnetic atoms per formula unit *)
3 (* Crystal field electronic contribution *)
1 (* Number of sites M1, M2, M3: maximum 3 sites *)
7 (* Number of Crystal field energy levels of the M1 site *)
2.000000000000000E+000 (* Number of atoms per formula unit having crystal-field splitting *)
1.63016083093689E-001 (* Magnetic correction factor (mf): Helmholtz A=na.RT.g(t).mf.ln(1+b) *)
Energy/cm^-1 Degeneracy Gruneisen parameter

0.000000E+000 3 0.000000E+000
2.407543E+001 3 0.000000E+000
5.057389E+001 3 0.000000E+000
1.058610E+003 3 0.000000E+000
1.058610E+003 3 0.000000E+000
1.000000E+004 5 0.000000E+000
1.000000E+004 5 0.000000E+000
Extra Free electron gas contribution
Cv(electronic)=Cv(crystal-Field)+a*T*(V/V0)^gamma_el
0.000000000000000E+000 (* Electronic Gruneisen parameter, gamma_el *)
0.000000000000000E+000 (* Electronic coefficient, a, in J/K/K/mol atoms that give crystal-field
1 (* 0=No cation disorder, 1=cation disorder: model of O'Neill and
Navrotsky*)
(* Hint=(h1+h2y)y, Sint=(s1+s2y)y: y=sitefraction metallic ion *)
1.20499320499321E+005 (* 1st Coefficient interchange enthalpy in J/mol *)
0.000000000000000E+000 (* 2st Coefficient interchange enthalpy in J/mol *)
0.000000000000000E+000 (* 1st Coefficient interchange entropy in J/K/mol *)
0.000000000000000E+000 (* 2st Coefficient interchange entropy in J/K/mol *)
1.000000000000000E+000 (* # moles of tetrahedral sites per molecular formula unit *)
2.000000000000000E+000 (* # moles of octahedral sites per molecular formula unit *)
0 (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &
Oganov 2007 Phys Rev B 75:024115 *)
Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
60 (* Number of Einstein modes *)
2 (* 1=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by
Stixrude & Lithgow-Bertelloni, 2005 *)
j Theta/K Fraction Gamma Mode_m(q) Gamma_inf a0 z

1 0.001439 0.000000000E+000 1.1604490 2.5068370 0.0000000 -2.670714E-005 0.0000000
2 18.401713 0.000000000E+000 1.1604490 2.5068370 0.0000000 -2.670714E-005 0.0000000
3 38.321393 9.499378026E-005 1.1604490 2.5068370 0.0000000 -2.670714E-005 0.0000000
.
60 1173.742446 3.437814992E-002 1.1604490 2.5068370 0.0000000 -2.670714E-005 0.0000000
#
sum of all fractions: 1.000000000E+000
#####
Isobaric calculation
1 (* 1=Isobaric calculation, 2=Isothermal calculation, 3=VDoS *)
0 2000 30 (* Temperature range and step: T_start/K, T_end/K, T_step/K *)
1e+05 1e+05 0.0 (* Pressure range and step : P_start/Pa, P_end/Pa, P_step/Pa *)
1 (* Output: 1=Output to screen and file, 0=Output to file only *)
Output file name
/home/michel/geodata/ringwoodite/fe-ringwoodite.out

```

## 16.2 Mono vacancies

We use a model outlined by Oganov and Dorogokupets (2007) to model mono vacancy defects in crystals. The expressions are:

### *Helmholtz energy*

$$A^{def}(T, V) = -\frac{3}{2} nRT \exp\left(s\eta^f - \frac{h\eta^g}{T}\right) \quad (17.1)$$

Values for  $f, g$  are  $f=-1$  and  $g=-2$  for the elements, C, Al, Au, Cu, Pt, Ta, W and for MgO. Variables  $h$  and  $s$  denote the enthalpy and entropy of formation of a mono vacancy. Parameter  $n$ , denotes the number of atoms in a molecular formula. Because the argument of the exponential is dimensionless, the unit of  $h$  is K and the parameter  $s$  is dimensionless. The compression,  $\eta$ , is  $V/V_0$ , where  $V_0$  is the volume at zero pressure and zero temperature and  $R$  is the gas constant.

### *Entropy*

$$S^{def}(T, V) = \frac{3}{2} nR \left(1 + \frac{h\eta^g}{T}\right) \exp\left(s\eta^f - \frac{h\eta^g}{T}\right) \quad (17.2)$$

### *Isochoric heat capacity*

$$C_V^{def}(T, V) = \frac{3}{2} nR \left(\frac{h\eta^g}{T}\right)^2 \exp\left(s\eta^f - \frac{h\eta^g}{T}\right) \quad (17.3)$$

### *Pressure contribution*

$$P^{def} = \frac{3}{2} \frac{nRT}{V} \left(s \cdot f \cdot \eta^f - \frac{h \cdot g \cdot \eta^g}{T}\right) \exp\left(s\eta^f - \frac{h\eta^g}{T}\right) \quad (17.4)$$

### *Temperature derivative of pressure*

$$\left(\frac{\partial P^{def}}{\partial T}\right)_V = \frac{3}{2} \frac{nR}{V} \left\{s \cdot f \cdot \eta^f + h \cdot \eta^g \left(\frac{s \cdot f \cdot \eta^f}{T} - \frac{h \cdot g \cdot \eta^g}{T^2}\right)\right\} \exp\left(s\eta^f - \frac{h\eta^g}{T}\right) \quad (17.5)$$

### *Isothermal bulk modulus*

$$K^{def}(T, V) = -\frac{3}{2} \frac{nRT}{V_0} \left\{s \cdot f \cdot (f-1)\eta^{f-1} - \frac{h \cdot g \cdot (g-1)\eta^{g-1}}{T} + \eta \left(s \cdot f \cdot \eta^{f-1} - \frac{h \cdot g \cdot \eta^{g-1}}{T}\right)^2\right\} \times \exp\left(s\eta^f - \frac{h\eta^g}{T}\right) \quad (17.6)$$

Note that in eqn. (17.6) we have divided by  $V_0$  and not by  $V$  as we did in the pressure contribution.

The input file below, for  $\text{Fe}_2\text{SiO}_4$  (fayalite) to be used in *'me'*, exemplifies the calculation of thermodynamic properties at 1 bar pressure between 0 and 1500 K in steps of 50 K. It can be extracted from file [mgsifeo-60-anh.mef](http://www.geo.uu.nl/~jacobs/Downloads), present on website <http://www.geo.uu.nl/~jacobs/Downloads>. The lines dealing with contributions to defects are given in blue.

```

<Fe2SiO4-oli> (* Name of the substance *)
203.776000 (* Mass of the substance in gr/mol *)
7.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-1.55169950972682E+006 (* Static lattice energy in J/mol *)
4.59885769248535E-005 (* Volume/m3/mol at zero K and zero Pa *)
4.57306725053928E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
2 (* l=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice
3 (* Order of Birch-Murnaghan EoS of the static lattice *)
1.430858000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
5.000000000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero Pa *)
5.465837000000000E+010 (* Static lattice shear modulus/Pa at zero Pa *)
1.426500000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero Pa *)
1.000000000000000E+000 (* Vibrational parameter of the shear modulus *)
0 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
1 (* 0=No magnetic contribution, 1=magnetic contribution *)
51 (* Magnetic: number of terms in the MacLaurin series expansion >2 *)
2.800000000000000E-001 (* Magnetic: Ratio Energy(tau>1)/total Energy for magnetic transition w
6.488000000000000E+001 (* Magnetic: Critical temperature Tc *)
4.000000000000000E+000 (* Magnetic: magnetic moment in Bohr magneton *)
3.000000000000000E+000 (* Magnetic: exponent (m) in Inden's (1981) expression for Cv below Tc
5.000000000000000E+000 (* Magnetic: exponent (n) in Inden's (1981) expression for Cv above Tc
2.000000000000000E+000 (* Magnetic: number of magnetic atoms per formula unit *)
3 (* Crystal field electronic contribution *)
2 (* Number of sites M1, M2, M3: maximum 3 sites *)
8 (* Number of Crystal field energy levels of the M1 site *)
5 (* Number of Crystal field energy levels of the M2 site *)
2.000000000000000E+000 (* Number of atoms per formula unit having crystal-field splitting *)
3.78868651539773E-001 (* Magnetic correction factor (mf): Helmholtz A=na.RT.g(t).mf.ln(1+b) *)
Energy/cm^-1 Degeneracy Gruneisen parameter

0.000000E+000 1 0.000000E+000
2.700000E+001 1 0.000000E+000
4.700000E+001 1 0.000000E+000
9.200000E+001 2 0.000000E+000
7.300000E+002 5 0.000000E+000
1.500000E+003 5 0.000000E+000
8.060000E+003 5 0.000000E+000
1.106000E+004 5 0.000000E+000
0.000000E+000 5 0.000000E+000
1.670000E+003 5 0.000000E+000
1.670000E+003 5 0.000000E+000
8.830000E+003 5 0.000000E+000
9.270000E+003 5 0.000000E+000
Extra Free electron gas contribution
Cv(electronic)=Cv(crystal-Field)+a*T*(V/V0)^gamma_el
0.000000000000000E+000 (* Electronic Gruneisen parameter, gamma_el *)
0.000000000000000E+000 (* Electronic coefficient, a, in J/K/K/mol atoms that give crystal-field
0 (* 0=No cation disorder, 1=cation disorder: model of O'Neill and Navrots
1 (* 0= No monovacancy defects, 1=monovacancy defects *)
(* Model: Dorogokupets & Oganov 2007 Phys Rev B 75:024115 *)
(* Helmholtz energy = -(3/2)nRT*exp(s*eta^f-h*eta^g/T) *)
(* with n=# atoms/formula unit, eta=V/V0 *)
8.167241300000000E+003 (* h: enthalpy of formation, K *)
0.000000000000000E+000 (* s: entropy, no unit *)
-1.000000000000000E+000 (* f *)
-5.000000000000000E-001 (* g *)
Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
60 (* Number of Einstein modes *)
2 (* l=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by
Stixrude & Lithgow-Bertelloni, 2005 *)
j Theta/K Fraction Gamma Mode_m(q) Gamma_inf a0 z

1 12.236857 0.0000000000E+000 1.6967220 1.8464070 0.0000000 -2.930085E-005 0.0000000
2 36.710135 0.0000000000E+000 1.6967220 1.8464070 0.0000000 -2.930085E-005 0.0000000
3 61.183573 7.925697191E-004 1.6967220 1.8464070 0.0000000 -2.930085E-005 0.0000000
.
59 1431.695444 5.442308366E-003 0.2916790 1.7895050 0.0000000 -2.930085E-005 0.0000000
60 1456.168896 1.651056381E-003 0.2916790 1.7895050 0.0000000 -2.930085E-005 0.0000000
#
sum of all fractions: 1.0000000000E+000
#####
Isobaric calculation
1 (* 1=Isobaric calculation, 2=Isothermal calculation, 3=VDoS *)
0 1500 50 (* Temperature range and step: T_start/K, T_end/K, T_step/K *)
1e+05 1e+05 0.0 (* Pressure range and step : P_start/Pa, P_end/Pa, P_step/Pa *)
1 (* Output: 1=Output to screen and file, 0=Output to file only *)
Output file name

```

/home/michel/geodata/fayalite/fayalite.out



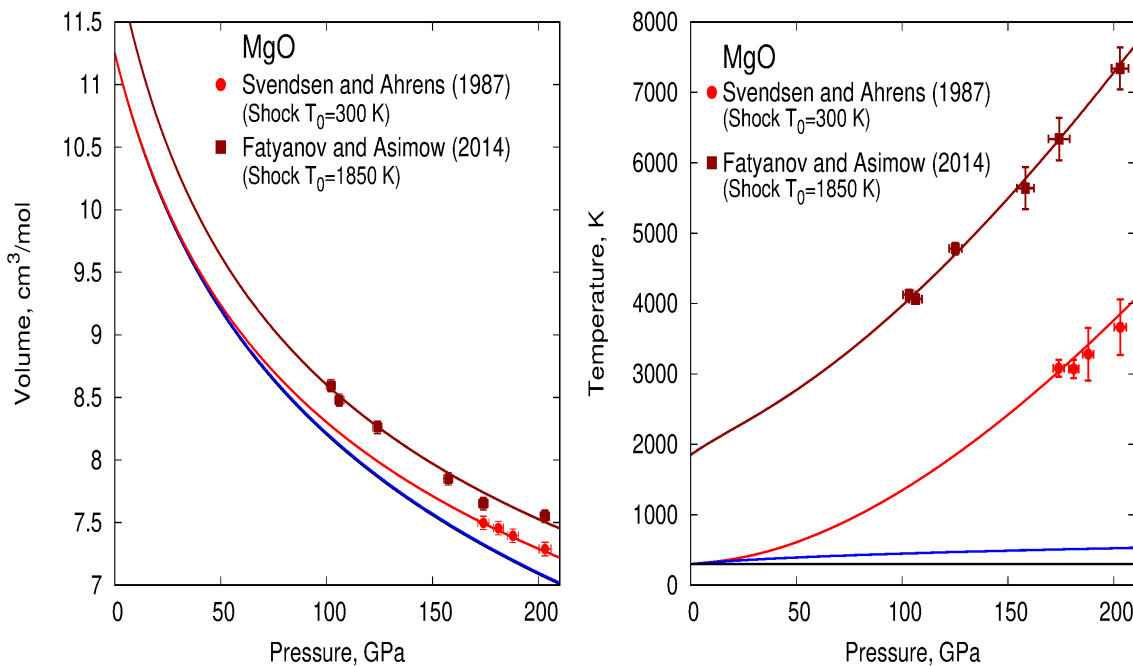
## 17 Hugoniot, isentropy

M.H.G. Jacobs, Institute of Metallurgy, TU-Clausthal, Germany, June 20<sup>th</sup>, 2020

Hugoniot data are obtained by subjecting a sample to planar shock waves. Because a large range of pressures and temperatures are covered by using shock wave techniques, the obtained data are extremely important for constraining the equation of state of substances. When the results of the measurements are on a Hugoniot, the Rankine-Hugoniot equations apply, which are based on conservation of mass, energy and momentum. Because of this characteristic the technique enables obtaining absolute compressibility data, and therefore it is possible to construct primary pressure scales. An overview of deriving equations of state of materials using shock-wave measurements is detailed by e.g. Ahrens (1993). The calculation of a Hugoniot path in  $P$ - $V$ - $T$  space with 'me' is based on the Rankin-Hugoniot expression:

$$U = U_0 + \frac{1}{2}(P + P_0)(V_0 - V) \quad (17.1)$$

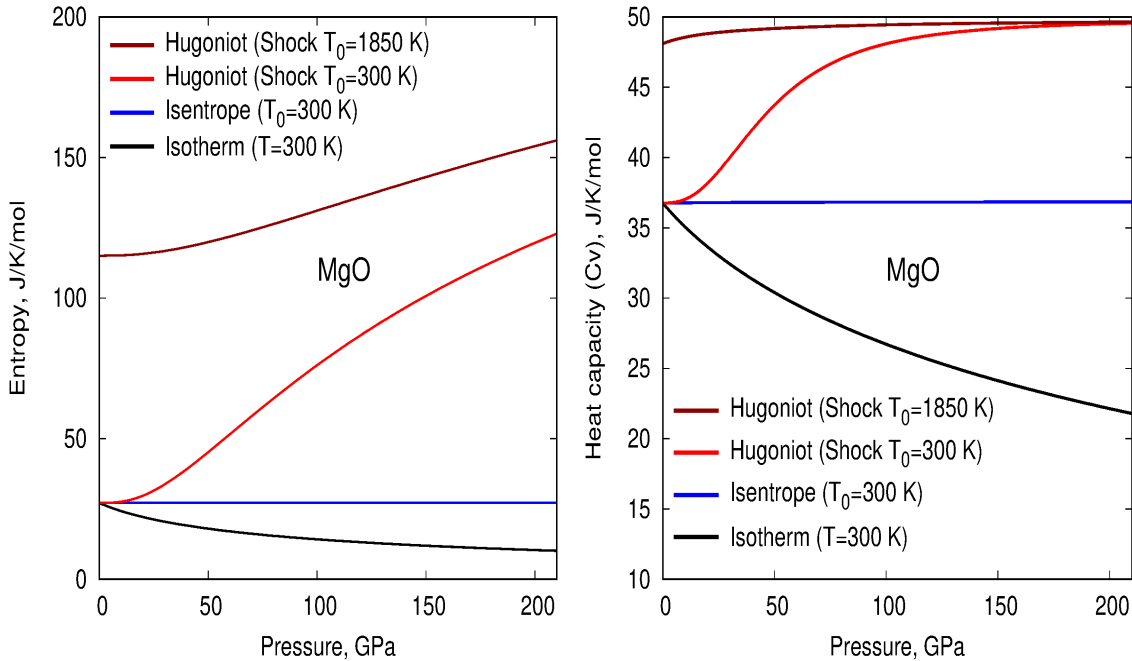
Energy  $U_0$ , pressure  $P_0$ , and volume  $V_0$  refer to initial conditions of the material. A characteristic of Hugoniots is that very large temperatures are achieved at large pressures, such as depicted for MgO in Figure 7.1. The figure also shows that different values for the initial temperature state of MgO were used by different investigators.



**Fig. 17.1.**  $V$ - $P$  and  $T$ - $P$  curves calculated along an isotherm at 300 K (black), isentrope with foot 300 K (blue) and Hugoniot (initial temperature 300 K in red and initial temperature 1850 K in dark-red). The MgO description has been obtained by Jacobs et al (2017) and is present in file [mgsifeo-60e-anh.mef](#). (see website <http://www.geo.uu.nl/~jacobs/Downloads>),

Temperatures on an isentrope are much smaller than on a Hugoniot and can be obtained by a shock-wave technique, such as described by Davis (2006). To calculate isentropes with 'me', an entropy must be selected. In Figure 7.1, the entropy of MgO at 300 K and 1 bar has been selected.

From the tables listed by 'me' it can be shown that thermodynamic properties on an isotherm, isentrope and Hugoniot, which all start at the same pressure and temperature, may differ greatly. An example for entropy and heat capacity is shown in Figure 17.2.



**Fig. 17.2.** Entropy (left) and isochoric heat capacity (right) along an isotherm at 300 K (black), isentrope with foot 300 K (blue) and Hugoniot (initial temperature 300 K in red and initial temperature 1850 K in dark-red). Entropy and heat capacity generally decrease with pressure along an isotherm. At pressures above 50 GPa, MgO behaves quasi-harmonically. Due to the high temperatures on the Hugoniot, vibrational modes become saturated, and  $C_v$  approaches the Dulong-Petit limit of  $3nR$ . The model description of MgO is the same as in Figure 17.1.

The input file used for the construction of Figures 17.1 and 17.2 is given in file [mgsifeo-60e-anh.mef](#). Making calculations on a Hugoniot or isentrope is indicated after the line containing "sum of all fractions". The lines controlling the calculations are given in blue.

```
<MgO-pc> (* Name of the substance *)
40.304000 (* Mass of the substance in gr/mol *)
2.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-6.21093534291483E+005 (* Static lattice energy in J/mol *)
1.12027710146365E-005 (* Volume/m3/mol at zero K and zero Pa *)
1.10736889124136E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
2 (* l=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice
3 (* Order of Birch-Murnaghan EoS of the static lattice *)
1.713650000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
4.185889000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero Pa *)
1.398012000000000E+011 (* Static lattice shear modulus/Pa at zero Pa *)
2.274201000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero Pa *)
2.068608000000000E+000 (* Vibrational parameter of the shear modulus *)
0 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
0 (* 0=No magnetic contribution, 1=magnetic contribution *)
0 (* No electronic contribution *)
0 (* 0=No cation disorder, 1=cation disorder: model of O'Neill & Navrotsky
0 (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets &
Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
60 (* Number of Einstein modes *)
2 (* l=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by Stix
j Theta/K Fraction Gamma Mode_m(q) Gamma_inf a0 z

1 8.511620 0.000000000E+000 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
```

```

2 25.534435 0.000000000E+000 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
.
.
59 995.842711 2.378020971E-003 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
60 1012.865744 6.061398740E-004 1.5153760 1.3987510 0.0000000 9.108297E-006 7.2990600
#
sum of all fractions: 1.0000000000E+000
#####
Hugoniot calculation
5 (* 1=Isobaric, 2=Isothermal, 3=VDoS, 4=Isentropic, 5=Hugoniot, 6=Clone
300 (* Temperature in Kelvin of the sample at 1 bar *)
1e+05 2.1e+11 1e+09 (* Pressure range and step : P_start/Pa, P_end/Pa, P_step/Pa *)
1 (* Output: 1=Output to screen and file, 0=Output to file only *)
Output file name
/home/michel/geodata/mgo/mgo-hugoniot-300.out

```

For the calculation of the isentrope given in Figure 17.1, substitute the lines behind "sum of all fractions..." by:

```

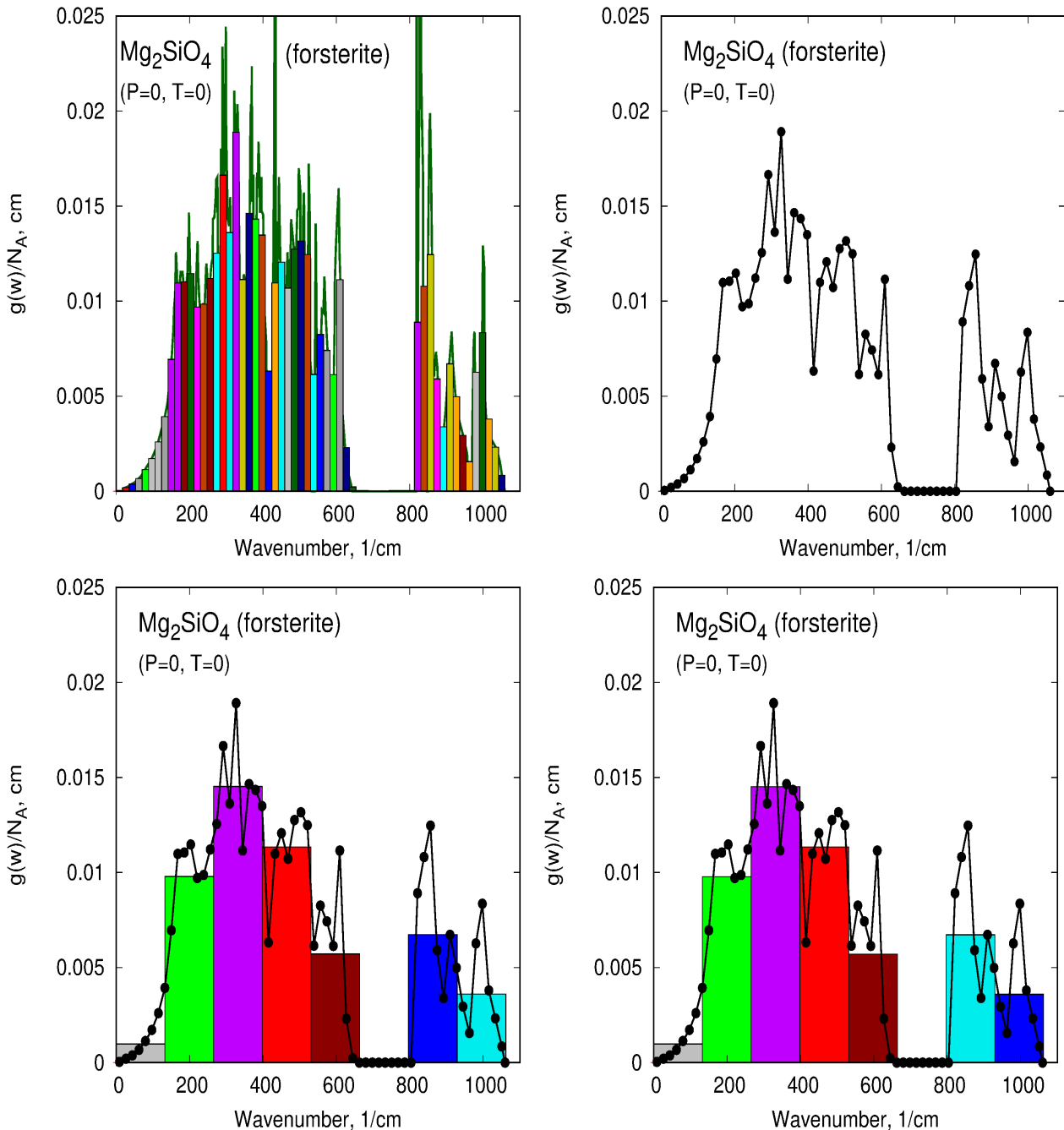
Isentropic calculation
4 (* 1=Isobaric, 2=Isothermal, 3=VDoS, 4=Isentropic, 5=Hugoniot, 6=Clone
27.1259 (* Constant entropy, J/K/mol *)
1e+05 2.1e+11 1e+09 (* Pressure range and step : P_start/Pa, P_end/Pa, P_step/Pa *)
1 (* Output: 1=Output to screen and file, 0=Output to file only *)
Output file name
/home/michel/geodata/mgo/mgo-isentrope-300.out

```

## 18 Database clones

M.H.G. Jacobs, Institute of Metallurgy, TU-Clausthal, Germany, June 20<sup>th</sup>, 2020

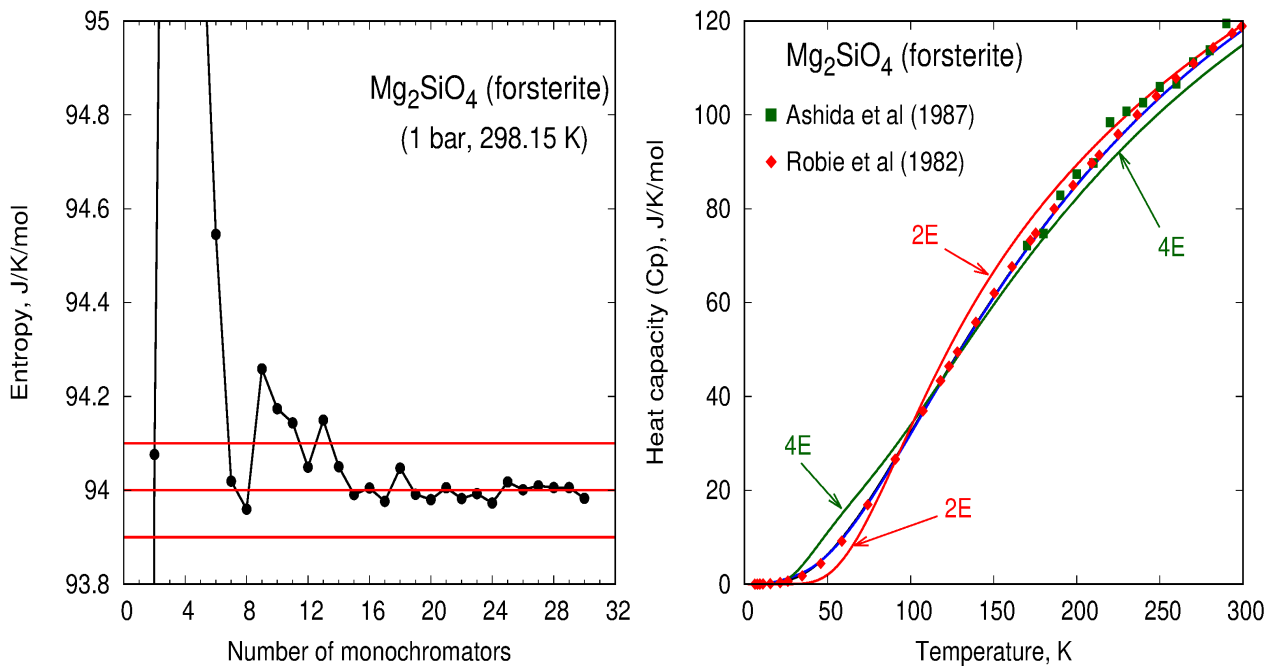
In some cases, such as for the benefit of increasing computational speed, one may wish to reduce the number of Einstein frequencies in the VDoS. Reducing the number of Einstein frequencies from 60 to 8 such as depicted in Figure 18.1, will result in a gain of a factor of about 5 in computational speed.



**Fig. 18.1.** Constructing a clone. **Top-left:** original VDoS with 60 Einstein frequencies representing ab initio results of Li et al (2007). The model description obtained by Jacobs et al (2017) is present in file [mgsifeo-60e-anh.mef](#). (see website <http://www.geo.uu.nl/~jacobs/Downloads>). **Top-right:** the mid points in the top of each Einstein box in the top-left frame are taken as 'new experimental points' for constructing a new VDoS. **Bottom-left:** these points are used to construct a VDoS with only 8 Einstein boxes. **Bottom-right:** the resulting VDoS in the bottom-left frame is stretched to match the entropy at the target condition.

In such a case '*me*' enables reducing the number of Einstein frequencies in the VDoS. In other words, the original model description is cloned to a new one. The construction of a cloned description is characterized by selecting the number of Einstein frequencies in the new VDoS and by selecting a target condition. The target condition specifies a point in  $P$ - $T$  space at which the enthalpy and entropy must have equal values as those calculated with the original description. Figure 18.1 shows how the clone process works.

A multiple-Einstein description of the VDoS consists of equidistantly spaced Einstein frequencies. Because one Einstein frequency is a line in the VDoS it difficult to compare the spectrum with a VDoS derived from ab initio predictions or inelastic neutron scattering experiments. Therefore it is depicted as a box (Einstein continuum in Kieffer's 1979 model) for which the surface is defined with a width equal to the distance between two subsequent Einstein frequencies and the fraction. Each Einstein frequency is located in the middle of each continuum. The surface under all the continua, thus obtained, is normalized to  $3nN_A$ , the degree of vibrational freedom. The top-left frame of Figure 18.1 shows the original VDoS of forsterite containing 60 Einstein frequencies. In the clone process, this VDoS is converted to a set to 60 points characterized by the frequency in the middle of each box and the top of the box, such as depicted in the top-right frame. In the bottom-left frame of Figure 18.1, eight frequencies were selected to construct a new VDoS. The width of each Einstein continuum is determined by the largest frequency occurring in the original VDoS,  $\sim 1100 \text{ cm}^{-1}$ . The height of each continuum (box) is determined by averaging the heights of points located within the frequency range of each continuum. To enhance accuracy, extra points may be inserted between two subsequent points in an automated process. At this stage entropy deviates significantly from that calculated with the original VDoS description at all temperatures and pressures. To keep entropy at the same value as determined with the original description at the target condition, the new VDoS is stretched or contracted in the frequency direction, using a minimization process. Finally, the enthalpy value is adjusted by changing the reference energy. Jacobs et al (2017) demonstrated that making calculations with a cloned description does not significantly affect phase diagrams and volume properties in many cases.



**Fig. 18.2.** **Left:** entropy  $S_{298.15}^{\circ}$  calculated with different number of Einstein frequencies in the VDoS and target condition 7.9 GPa, 1173 K. The horizontal lines indicate the experimental value of  $94 \pm 0.1 \text{ J/K/mol}$  obtained by Dachs et al (2007). **Right:** low temperature heat capacity data are represented with the original description and that with 8 frequencies in the VDoS, but not with 2 or 4 frequencies in the VDoS.

A target condition of 7.9 GPa and 1173 K has been taken for constructing the VDoS in Figure 18.1. The right-hand frame of Figure 18.2 shows that matching the entropy at such high temperature goes at the expense of accuracy in heat capacity and therefore entropy at lower temperatures.

Figure 18.2 shows that clones having 14 or more Einstein frequencies in the VDoS have an ambient entropy that matches the experimental value determined by Dachs et al (2007). These descriptions do not show significant deviations of all thermodynamic properties relative to those obtained with the original description. These clones are therefore safe to use in the P-T stability range of forsterite. From investigations of substances and solid solution phases in the system MgO-SiO<sub>2</sub>-FeO, it appears that for most substances a minimum of about 14 Einstein frequencies is needed to produce results insignificantly different from the original description. That also holds for MgO when very high temperatures and pressures are investigated located on the Hugoniot, depicted in Figure 17.1. For metals having a VDoS, which extends in a much smaller frequency range compared to silicates, a smaller number of Einstein frequencies is sufficient, typically between 2 and 5.

The right-frame of Figure 18.2 shows for forsterite that clones having 12, 8, 7 and 2 Einstein frequencies in the VDoS also produce an acceptable value for the ambient entropy. The right-frame of Figure 18.2 shows that heat capacity calculated with a clone having 8 Einstein frequencies in the VDoS produce results that are insignificantly different from the original description. That also holds for other thermodynamic properties. However this is not the case for 4 or 2 Einstein frequencies in the VDoS.

An example for constructing a clone with 'me', copied from [mgsifeo-60e-anh.sag](http://www.geo.uu.nl/~jacobs/Downloads) downloadable from website <http://www.geo.uu.nl/~jacobs/Downloads> is given below. The lines controlling the calculations are given in blue.

```

<Mg2SiO4-oli> (* Name of the substance *)
 140.692000 (* Mass of the substance in gr/mol *)
 7.000000000000000E+000 (* Number of atoms in 1 molecular formula unit *)
-2.25175662911328E+006 (* Static lattice energy in J/mol *)
 4.34970344652468E-005 (* Volume/m3/mol at zero K and zero Pa *)
 4.30816682094395E-005 (* Volume/m3/mol of the static lattice at zero Pa *)
 2 (* l=Vinet, 2=Birch-Murnaghan, 3=Keane, 4=Qin EoS of the static lattice
 3 (* Order of Birch-Murnaghan EoS of the static lattice *)
 1.350423000000000E+011 (* Static lattice bulk modulus/Pa at zero Pa *)
 4.180000000000000E+000 (* Pressure derivative of the static lattice bulk modulus at zero Pa *)
 8.718426000000000E+010 (* Static lattice shear modulus/Pa at zero Pa *)
 1.498445000000000E+000 (* Pressure derivative of the static lattice shear modulus at zero Pa *)
 1.915333000000000E+000 (* Vibrational parameter of the shear modulus *)
 0 (* 0=No Landau contribution, 1=2nd order, 2=Tricritical, 3=1st order *)
 0 (* 0=No magnetic contribution, 1=magnetic contribution *)
 0 (* No electronic contribution *)
 0 (* 0=No cation disorder, 1=cation disorder: model of O'Neill and Navro
 0 (* 0=No monovacancy defects, 1=monovacancy defects: Dorogokupets & Ogan
Anharmonicity is described with perturbation theory of Oganov & Dorogokupets (2004): a=a0(V/V0)^z
 60 (* Number of Einstein modes *)
 2 (* l=Gruneisen expression by Al'tshuler et al, 1987 and 2=that by Stixr
j Theta/K Fraction Gamma Mode_m(q) Gamma_inf a0 z

 1 12.997527 1.009823583E-004 1.2901120 1.7857310 0.0000000 -8.650911E-006 0.0000000
 2 38.404252 4.938673280E-004 1.2901120 1.7857310 0.0000000 -8.650911E-006 0.0000000
.
.
.
60 1512.002075 2.139388114E-003 0.4500000 0.0000000 0.0000000 -8.650911E-006 0.0000000
#
sum of all fractions: 1.000000000E+000
#####
Cloning a VDoS to a VDoS with a smaller number of Einstein frequencies
6 (* l=Isobaric, 2=Isothermal, 3=VDoS, 4=Isentropic, 5=Hugoniot, 6=Clone *)
8 (* Desired number of Einstein frequencies in the VDoS *)
7.9e+09 1173 (* Clone condition P/Pa, T/K at which enthalpy and entropy must remain
 unchanged *)
Output file name
/home/michel/geodata/mgo/mgo-8-clone.mef

```

## Version, features and units

M.H.G. Jacobs, Institute of Metallurgy, TU-Clausthal, Germany, July 1<sup>st</sup>, 2021

| Version | Features                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | Unit(s)                                                                       |
|---------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| All     | Controlling all units                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Me.pas                                                                        |
| All     | Declaring types and variables, initializing variables, frequently used functions                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | Variables.pas                                                                 |
| All     | Reading input files, frequently used procedures                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | Readinput.pas                                                                 |
| 1       | <u>Frequency/Grüneisen expressions according to</u><br>1. Al'tshuler LV, Brusnikin SE, Kuz'menkov EA (1987) J Appl Mech Tech Phys 28:129-141<br>2. Stixrude L, Lithgow-Bertelloni (2005) Geophys J Int 162:610-632<br><u>Static Equations of State</u><br>1. Up to 8 <sup>th</sup> order Birch-Murnaghan<br>2. 3 <sup>rd</sup> order Vinet<br>3. Keane's (1954) Equation of State (version $\geq 9$ )<br>4. Qin et al (2008) Equation of State (version $\geq 9$ )<br><u>Electronic contribution</u><br>1. Free electron gas electronic contribution | Vibrations.pas<br>Static.pas<br>Electronic.pas<br>Maketable<br>Makevolume.pas |
| 2       | Landau formalism: 1 <sup>st</sup> order, 2 <sup>nd</sup> order, tricritical<br>Magnetic contribution                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Landaucalc.pas<br>Magnetic.pas                                                |
| 3       | Crystal-Field electronic contribution                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Electronic.pas                                                                |
| 4       | Making GnuPlot files for plotting VDoS<br>Making 'me' input file from an abinitio VDoS                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Plotvdos.pas<br>Medos.pas                                                     |
| 5       | Cation disorder                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | Cationdisorder.pas                                                            |
| 6       | Mono vacancy defects                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Defects.pas                                                                   |
| 7       | OS: Linux, Windows                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                               |
| 8       | Hugoniot, Isentrope, cloning                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | Isenhugo.pas<br>Savemef.pas                                                   |

## References

- Ahrens TJ (1993) Equation of State. in High Pressure Shock Compression of Solids, Chapter 4, eds J.R. Asay and M. Shahinpoor, Springer-Verlag, NY, 75-114
- Anderson OL (1998) Equations of State of Solids for Geophysics and Ceramic Science. Oxford Monographs on Geology and Geophysics No 31, New York, Oxford, Oxford University Press, p163
- Aronson MC, Stixrude L, Davis MK, Gannon W, Ahilan K (2007) Magnetic excitations and heat capacity of fayalite,  $\text{Fe}_2\text{SiO}_4$ . *Am Mineral* 92:481-490
- Ashida T, Kume S, Ito E (1987) Thermodynamic aspects of phase boundary among  $\alpha$ -,  $\beta$ -, and  $\gamma$ - $\text{Mg}_2\text{SiO}_4$ . In Manghnani MH, Syono Y (eds) High Pressure Research in mineral physics. Terra Scientific Publishing Company (TERRAPUB), Tokyo/American Geophysical Union, Washington, pp 269-274
- Birch F (1952) Elasticity and constitution of the Earth's interior. *J Geophys Res* 57:227-286
- Burns RG (1985) Thermodynamic data from crystal field spectra. Microscopic to macroscopic-atomic environments to mineral thermodynamics. *Rev Mineral* 14:277-316
- Carpenter MA (1992) Thermodynamics of phase transitions in minerals: a macroscopic approach. In: Stability of minerals GD Price and NL Ross (Eds) Chapman & Hall
- Dachs E, Geiger CA, Seckendorff von V, Grodzicki M (2007) A low-temperature study of synthetic (forsterite + fayalite) [ $\text{Mg}_2\text{SiO}_4 + \text{Fe}_2\text{SiO}_4$ ] solid solutions: An analysis of vibrational, magnetic, and electronic contributions to the molar heat capacity and entropy of mixing. *J Chem Thermodyn* 39:906-933
- Davis J-P (2006) Experimental measurement of the principal isentrope for aluminum 6061-T6 to 240 GPa. *J Appl Phys* 88:103512
- Dinsdale AT (1991) SGTE data for pure elements. *Calphad* 15:317-425
- Dorogokupets PI, Oganov AR (2007) Ruby, metals, and MgO as alternative pressure scales: A semiempirical description of shock-wave, ultrasonic, x-ray, and thermochemical data at high temperatures and pressures. *Phys Rev B* 75:024115
- Fat'yanov OV, Asimow PD (2014) MgO melting curve constraints from shock temperature and rarefaction overtake measurements in samples preheated to 2300 K. *Journal of Physics: Conference Series* 500, 062003:1-6
- Gopal ESR (1966) Specific heats at low temperatures. Plenum Press New York
- Hillert M, and Jarl M (1979) A model for alloying effects in ferromagnetic metals. *Calphad* 2:227-228
- Hofmeister AM (1987) Single-crystal absorption and reflection infrared spectroscopy of forsterite and fayalite. *Phys Chem Minerals* 14:499-513
- Holland TJB, Powell R (1998) An internally consistent thermodynamic data set for phases of petrological interest. *J Metamorphic Geol* 16:309-343
- Inden G (1981) The role of magnetism in the calculation of phase diagrams. *Physica* 103B:82-100
- Jacobs MHG, de Jong BHWS (2009) Thermodynamic mixing properties of olivine derived from lattice vibrations. *Phys Chem Minerals* 36:365-389
- Jacobs MHG, Schmid-Fetzer R (2010) Thermodynamic properties and equation of state of fcc aluminium and bcc iron, derived from a lattice vibrational method. *Phys Chem Minerals* 37:721-739
- Jacobs MHG, Schmid-Fetzer R, Van den Berg AP (2013) An alternative use of Kieffer's lattice dynamics model using vibrational densities of states for constructing thermodynamic databases. *Phys Chem Minerals* 40:207-227
- Jacobs MHG, Schmid-Fetzer R, Van den Berg AP (2017) Phase diagrams, thermodynamic properties and sound velocities derived from a multiple Einstein method using Vibrational Densities of States: An application to  $\text{MgO-SiO}_2$ . *Phys Chem Minerals* 44:43-62
- Jacobs MHG, Schmid-Fetzer R, van den Berg AP (2019) Thermophysical properties and phase



- diagrams in the system MgO-SiO<sub>2</sub>-FeO at upper mantle and transition zone conditions derived from a multiple-Einstein method. *Phys Chem Minerals* 46:513-534
- Keane A (1954) An investigation of finite strain in an isotropic material subjected to hydrostatic pressure and its seismological applications. *Aust J Phys* 7:322-333
- Kieffer SW (1979) Thermodynamics and lattice vibrations of minerals: 3. Lattice dynamics and an approximation for minerals with application to simple substances and frameworks silicates. *Rev Geophys Space Phys* 17:35-59
- Kittel C (1996) *Introduction to solid state physics*. John Wiley and Sons, New York
- Li L, Wentzcovitch RM, Weidner DJ, Da Silva CR (2007) Vibrational and thermodynamic properties of forsterite at mantle conditions. *J Geophys Res* B112:05206
- Navrotsky A, Kleppa OJ (1967) The thermodynamics of cation distributions in simple spinels. *J Inorg Nucl Chem* 29:2701-2714
- Navrotsky A (1977) Calculation of effect of cation disorder on silicate spinel phase boundaries. *Earth Planet Sci Lett* 33:437-442
- Navrotsky A. (1994) *Physics and Chemistry of Earth Minerals*, Cambridge University Press, 1994.
- Oganov AR, Gillan MJ, Price CD (2005) Structural stability of silica at high pressures and temperatures. *Phys Rev B* 71:064104, 1-8
- O'Neill HStC, Navrotsky A (1983) Simple spinels: crystallographic parameters, cation radii, lattice energies, and cation distribution. *Am Mineral* 68:181-194
- O'Neill HStC, Navrotsky A (1984) Cation distributions and thermodynamic properties of binary spinel solid solutions. *Am Mineral* 69:733-753
- Putnis A (1992) *Introduction to Mineral Sciences*. Cambridge University Press, Cambridge
- Qin T, Drautz R, Pettifor DG (2008) Equation of state for transition metals. *Phys Rev B* 77:220103(R)
- Robie RA, Hemingway BS, Takei H (1982) Heat capacities and entropies of Mg<sub>2</sub>SiO<sub>4</sub>, Mn<sub>2</sub>SiO<sub>4</sub> and Co<sub>2</sub>SiO<sub>4</sub> between 5 and 380 K. *Am Miner* 67:470-482
- Schrettle F, Kant Ch, Lunkenheimer P, Mayr F, Deisenhofer J, Loidl A (2012) Wüstite: electric, thermodynamic and optical properties of FeO. *Eur Phys J B* 85:164 (12pp)
- Stixrude L, Lithgow-Bertelloni (2005) Thermodynamics of mantle minerals – I. Physical properties. *Geophys J Int* 162:610-632
- Svendsen B, Ahrens TJ (1987) Shock-induced temperatures of MgO. *Geophys J R astr Soc* 91:667-691
- Tsuchiya T, Kawamura K (2002) First-principles electronic thermal pressure of metal Au and Pt. *Phys Rev B* 66:094115
- Vinet P, Ferrante J, Rose JH, Smith JR (1987) Compressibility of solids. *J Geophys Res* 92:9319-9325
- Vinet P, Ferrante J, Rose JH, Smith JR (1989) Universal features of the equation of state of solids. *J Phys Condens Matter* 1:1941-1963
- Wu Z, Justo JF, da Silva CRS, de Gironcoli S, Wentzcovitch RM (2009) Anomalous thermodynamic properties in ferropericlae throughout its spin crossover. *Phys Rev B* 80:014409
- Yu YG, Wentzcovitch RM (2006) Density functional study of vibrational and thermodynamic properties of ringwoodite. *J Geophys Res* 111:B12202, 1-8
- Yu Y, Vinograd VL, Winkler B, Wentzcovitch RM (2013) Phase equilibria of (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> at the Earth's upper mantle conditions from first-principles studies. *Phys Earth Plan int* 217:35-47