Thermodynamics in high-temperature pressure scales on example of MgO

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Abstract. The simplest equation within the framework of the Mie-Grüneisen-Einstein approach is considered, which offers the calculation of pressure as a function of temperature and volume, by the use of simple arithmetic and algebraic operations. This equation coincides with the Mie-Grüneisen-Debye model at high temperature. Various versions of the Speziale et al. (2001) equation of state of MgO that were recently used as the pressure standard at high temperatures have been analyzed. In the literature we have found no less than three versions of the Speziale et al. (2001) EoS of MgO: Hirose et al. (2008), Wu et al. (2008), Zha et al. (2008), the discrepancy between them reaching a few GPa. The analysis of various versions of the Speziale et al. (2001) EoS of MgO shows that the volume dependence of the Debye temperature is accepted arbitrarily, which does not agree with the definition of the Grüneisen parameter, $\gamma = -\left(\frac{\partial \ln \Theta}{\partial \ln V}\right)_T$.

1. Introduction
The Speziale et al. [1] equation of state (EoS) of MgO is currently used as an actual pressure standard at high temperature (Fei et al. [2]; Hirose et al. [3], [4]; Komabayashi et al. [5]; Zha et al. [6]; Tateno et al. [7]; etc.). This equation of state of MgO has been constructed within the framework of the Mie-Grüneisen-Debye assumptions, it well describes the low-pressure XRD data on the volume of MgO to 52 GPa and the shock-wave data to 203 GPa. However, using the Speziale et al. [1] EoS of MgO as a standard of pressure it is necessary to consider the following: 1) Guignot et al. [8] have noted that the Speziale et al. [1] EoS of MgO overestimates the thermal pressure by a few GPa. 2) Dorogokupets and Dewaele [9] have shown that the Speziale et al. [1] EoS of MgO is not thermodynamically justified, since they used only static and shock-wave measurements without taking into account the thermodynamic data at room pressure and at high temperatures ($C_p$, $\alpha$, $K_S$). 3) In the Wu et al. [10] paper, the $P-V-T$ data for MgO, calculated with Speziale et al. [1] EoS of MgO are given, which do not coincide with our calculations at high temperatures (see table 5 in [9] and table 3 in [10]). The difference exceeds 1 GPa at 3000 K, that is inadmissible for pressure scales if calculations are carried out on the same model. 4) There is one more version of the Speziale et al. [1] EoS of MgO which is used in [4, 5, 7], but it differs from Wu et al. [10] and Zha et al. [6] versions, that will be shown below.

We shall consider the simplest equation within the framework of the Mie-Grüneisen-Einstein model which lets us calculate pressure as a function of temperature and volume using the simple arithmetic and algebraic operations. This EOS coincides with the Mie-Grüneisen-Debye model at high temperature. Further we shall use this equation for the analysis of calculated and experimental $P-V-T$ data of MgO.
2. Equations of state of MgO

2.1. Speziale et al. [1] EoSs of MgO in the Mie-Grüneisen-Einstein approach

At high temperature, \( T > \Theta_D/2 \) \([11]\), the quasiharmonic phonon part of the Helmholtz free energy in the Debye approach (e.g. \([12, 13, 14, 9]\), etc.) can be replaced by the Einstein model, \( F_{qh} = 3nR T \ln[1 - \exp(-\Theta/T)] \), without loss of accuracy. Differentiating this expression on volume and adding room-temperature isotherm and anharmonicity pressure we receive pressure in the Mie-Grüneisen-Einstein approach:

\[
P(V, T)(\text{GPa}) = \frac{3}{2} K_0 \left( x^{-7/3} - x^{-5/3} \right) \times \left[ 1 - \frac{3}{4} (4 - K') \left( x^{-2/3} - 1 \right) \right]
\]

\[+ 3nR \left[ \frac{\Theta}{\exp(\Theta/T) - 1} - \frac{\Theta}{\exp(\Theta/T_0) - 1} \right] \frac{\gamma}{xV_0} \times 10^{-3},\]

\[+ \frac{3}{2} n R a_0 x^n \left( T^2 - T_0^2 \right) \frac{m}{xV_0} \times 10^{-3},\]

where the first line is a third-order Birch-Murnaghan equation, the second line is the quasiharmonic pressure in the Einstein approach, and the third line is the contribution of intrinsic anharmonicity to pressure (see \([9, 15]\), \( K_0 \) (GPa) is isothermal bulk modulus, \( K' = dK_0/dP \), \( x = V/V_0 \), \( V_0 \) (cm\(^3\)) is volume at reference condition, \( R = 8.31451 \) J mol\(^{-1}\) K\(^{-1}\) is the gas constant, \( n \) is the number of atoms per a unit cell (\( n = 2 \) for MgO), \( \Theta \) is the Einstein temperature depending on volume, which correspond with the Debye temperature as \( \Theta_E = \Theta_D \times 3/5 = 0.775 \times \Theta_D \), \( T_0 \) is reference temperature (298.15 K), \( a_0 \) (K) and \( m \) are anharmonicity parameters. At differentiation \( \Theta \) the logarithmic derivative appeared, \( \gamma = -\left( \partial \ln \Theta / \partial \ln V \right) \), which is the definition of the Grüneisen parameter. Volume dependence of the Debye (Einstein) temperature and the Grüneisen parameter can be written in a classical form \([1]\):

\[
\Theta = \Theta_0 \exp \frac{\gamma_0 (1 - x^{q_0})}{q_0}, \quad \gamma = \gamma_0 x^{q_0}.
\]

Speziale et al. [1] have considered two equations of state of MgO. The first is a classical Mie-Grüneisen-Debye equation which can be precisely described by the equations (1) and (2) (see Table 1, Fit # 1). These equations on the 3000 K isotherm give the following pressure: 17.69 GPa at \( x = 1 \), 51.69 GPa at \( x = 0.85 \), and 190.72 GPa at \( x = 0.64 \) and \( T = 3663 \) K, that coincides with the pressure plotted in Fig. 6 in [1]. But these pressures are much lower than those deduced from the shock-wave data \([16]\).

Speziale et al. [1] have carefully analyzed the volume dependence of the Grüneisen parameter, and determined that \( q_0 = 1.65 \) from thermodynamic relations at ambient conditions and also that \( q \) approaches zero at high compression. Speziale et al. [1] assumed the volume dependence of the Grüneisen parameter as \([17]\)

\[
\gamma = -\left( \frac{\partial \ln \Theta}{\partial \ln V} \right)_T = \gamma_0 \exp \left[ \frac{d_0 \left( x^{q_0} - 1 \right)}{q_1 x^{q_0}} \right],
\]

\[
q = -\left( \frac{\partial \ln \gamma}{\partial \ln V} \right)_T = q_0 x^{q_0},
\]

with \( q_0 = 1.65 \) and \( q_1 = 11.8 \).

Debye temperature cannot be calculated from the equation (3) in an analytical form, though it can be calculated numerically. Probably, because of this various versions of the Speziale et al. [1] EoS of MgO, used as pressure scales, have been obtained.

We used the Al'tshuler et al. [18] form for the volume dependence of the Debye (Einstein) temperature and the Grüneisen parameter:

\[
\Theta = \Theta_0 x^{\gamma_0} \exp \left[ \frac{\gamma_0 - \gamma}{\beta} (1 - x^{\beta}) \right], \quad \gamma = \gamma_0 + (\gamma_0 - \gamma_0 x^{\beta}), \quad q = \beta x^{\beta} \frac{\gamma_0 - \gamma}{\gamma}.
\]
where $\gamma_0$ is the Grüneisen parameter at ambient conditions, $\gamma_\infty$ is the Grüneisen parameter at infinite compression ($x = 0$), and $\beta$ is a fitted parameter.

Equation (5) with parameters $\gamma_\infty = 1.325$ and $\beta = 11.8$ at compression from $x = 1$ to $x = 0.6$ with accuracy within 0.3% approximates the Grüneisen parameter calculated from equation (3) with $q_0 = 1.65$ and $q_1 = 11.8$. Hence, we can calculate volume dependence of the Debye (Einstein) temperature and the Grüneisen parameter from equations (5) and then calculate pressure from equation (1).

Thus, we have received the second equation, which should be used as a true pressure scale of Speziale et al. [1] (see table 1, Fit # 2). But now for the 3000 K isotherm we obtain pressure 17.69 GPa at $x = 1$, and 54.21 GPa at $x = 0.85$. At temperature 3663 K and compression $x = 0.64$ we obtain pressure equal to 203.34 GPa, whereas Speziale et al. [1] on inset figure 6 show pressure near 207 GPa when $q = 0$. In our version of Speziale et al. [1] EoS at high compression the $q$ parameter is close to zero also, and we do not find explanation of distinction in pressure other than a mistake in the Speziale et al. [1] EoS of MgO.

However, it is necessary to notice, that the received true Speziale et al. [1] EoS becomes unstable at temperatures higher than 2200 K at ambient pressure. This means, that there is no $x$ that corresponds to the atmospheric pressure from equations (1) and (5) at temperatures above 2200 K. For this reason, Dorogokupets and Dewaele [9] used the equation (5) with parameters $\gamma_\infty = 1.32$ and $\beta = 7.3$ to reproduce Speziale et al. [1] EoS of MgO.

### Table 1. Parameters of the published EoSs of MgO

| Parameters | Fit # 1 | Fit # 2 | Fit # 3 | Fit # 4 | Fit # 5 | Fit # 6 |
|------------|--------|--------|--------|--------|--------|--------|
| $V_0$ (cm³) | 11.248 | 11.248 | 11.248 | 11.248 | 11.248 | 11.248 |
| $K_0$ (GPa) | 160.2 | 160.2 | 160.2 | 160.2 | 162.2 | 160.64 |
| $K'$ | 3.99 | 3.99 | 3.99 | 3.99 | 4.23 | 4.221 |
| $\Theta_0$ (K) | 599 | 599 | 630=const | 599 | 621 | 589 |
| $\gamma_0$ | 1.524 | 1.524 | 1.524 | 1.433 | 1.520 | 1.431 |
| $\beta$ or $q_0$ | 1.65 | 11.8 | 11.648 | -0.163 | 1.406 | 3.50 |
| $\gamma_\infty$ | 0 | 1.325 | 1.318 | 0.108 | 0.606 | 1.016 |
| $a_0$ ($10^{-6}$ K⁻¹) | – | – | – | – | -15.4 | – |
| $m$ | – | – | – | – | 1.75 | – |

Fit # 1: $V_0$, $K_0$, $K'$, $\gamma_0$ and $q_0$ from Speziale et al. [1]. $\Theta_0$ is the Einstein temperature calculated from Debye temperature 773 K.

Fit # 2: $V_0$, $K_0$, $K'$ and $\gamma_0$ from Speziale et al. [1], $\beta$ and $\gamma_\infty$ are fitted parameters (see text).

Fit # 3: $V_0$, $K_0$, $K'$ and $\gamma_0$ from Speziale et al. [1], $\beta$ and $\gamma_\infty$ are fitted parameters of $P$-$V$-$T$ data published in Wu et al. (2008), $\Theta_0$ = const.

Fit # 4: $V_0$, $K_0$, and $K'$ from Speziale et al. [1], $\gamma_0$, $\beta$ and $\gamma_\infty$ are fitted parameters of $P$-$V$-$T$ data published in [3, 4, 5, 2].

Fit # 5: fit of the Wu et al. [10] EoS of MgO using equations (1) and (5).

Fit # 6: Tange et al. [19] EoS of MgO.

### 2.2. Other versions of the Speziale et al. [1] EoS of MgO

Unfortunately, $P$-$V$-$T$ data for MgO are not published by Speziale et al. [1], therefore further we shall compare alternative $P$-$V$-$T$ data, which are shown in table 3 by Wu et al. [10], and also in [2, 3, 4, 5, 7]. Figure 1 shows a difference between pressure resulted in [2, 4, 5, 7, 10] and our calculation. All alternative tabulations of Speziale et al. [1] EoS of MgO essentially overestimate the pressure in comparison with our version (Fit # 2). The deviations reach 4.5 GPa at temperature near 4000 K which are achieved by Tateno et al. [7]. However, as shown in figure 1, there is a version of Speziale et al. [1] EoS of MgO which is used by Zha et al. [6] and is close to our version (Table 1, Fit # 2).
What are alternative tabulations of the Speziale et al. [1] EoS of MgO? We assume, that in the tabulation by Wu et al. [10] the volume dependence of the Debye temperature is likely considered to be constant, which is not correct. If $\Theta = \Theta_0 = 630$ K = const, than, fitting $\beta$ and $\gamma_\infty$ (Table 1, Fit # 3), we receive the equation which well fits $P-V-T$ data from table 3 [10]. The quality of the fit is illustrated in figure 2a. We have not received an exact description of $P-V-T$ data, however, almost all discrepancies are within ±0.05 GPa. Hence, our assumption seems to be correct.

**Figure 1.** Difference in pressure between $P-V-T$ points calculated using different versions of Speziale et al. [1] EoS of MgO (Hirose et al. [4]; Fei et al. [2]; Komabayashi et al. [5]; Tateno et al. [7]; Wu et al. [10]; Zha et al. [6]) and calculated from our reconstruction of Speziale et al. [1] EoS of MgO (Table 1, Fit # 2).

**Figure 2.** Difference in pressure between published EoS of MgO and our calculations.
(a) $P-V-T$ data from Table 3 by Wu et al. [10], $V_0$, $K_0$, $K'$ and $\gamma_0$ from Speziale et al. [1], $\beta$ and $\gamma_\infty$ are fitted parameters, $\Theta = \Theta_0 = 630$ K = const, (Table 1, Fit # 3).
(b) $P-V-T$ data from (Hirose et al. [3, 4]; Komabayashi et al. [5]; Fei et al. [2]; Tateno et al. [7]), $V_0$, $K_0$, and $K'$ from Speziale et al. [1], $\gamma_0$, $\beta$ and $\gamma_\infty$ are fitted parameters (Table 1, Fit # 4).
(c) $P-V-T$ data from Wu et al. [10] EoS of MgO, all parameters are fitted (Table 1, Fit # 5).
We also have restored the equation of state of MgO which was used in Hirose et al. [4], Komabayashi et al. [5], and Tateno et al. [7] papers. It looks somewhat strange because parameters $\beta$ and $\gamma_\infty$ have unrealistically low values (Table 1, Fit # 4), nevertheless, quite satisfactory (Figure 2b) describes the $P$-$V$-$T$ data from those papers.

2.3. Wu et al. [10] and Tange et al. [19] EoSs of MgO

Wu et al. [10] have constructed their own equation of state of MgO, which was obtained by combining first principles local density approximation quasi-harmonic (QHA) calculations with experimental low-pressure data and agrees very well with shock compression data. The $P$-$V$-$T$ data from Wu et al. [10] EoS of MgO are very well described by the equation (1) with parameters from table 1 (Fit # 5) up to pressure 150 GPa using the third-order Birch-Murnaghan equation instead of the fourth-order Birch-Murnaghan equation in Wu et al. [10] EoS (Figure 2c).

Tange et al. [19] have constructed the equation of state of MgO in the Mie-Grüneisen-Debye approach by processing the $P$-$V$-$T$-$K_s$ data up to 196 GPa and 3700 K. They have simply rearranged Al'tshuler et al. [18] volume dependence of the Grüneisen parameter to form $\gamma = \gamma_0 [1 + a (x - 1)]$, which coincides with the equation (5) if $b = \beta$ and $\gamma_\infty = \gamma_0 (1 - a)$. The parameters of the Tange et al. [19] EoS of MgO in the Mie-Grüneisen-Einstein approach are given in table 1.

Note, that the room-temperature isotherms from Wu et al. [10] and Tange et al. [19] EoSs of MgO agree well with Speziale et al. [1] measurements, recalibrated using new ruby pressure scales (Dorogokupets and Oganov [20, 21]; Syassen [22]; Dewaele et al. [23]; etc.). However, they overestimate pressure by up to 2.5–3 GPa (Tange et al. [19]) and up to 3.5–4 GPa (Wu et al. [10]) at 100 GPa in comparison with Jacobsen et al. [24] measurements, recalibrated using new ruby pressure scales.

3. Concluding remarks

We suggest to use the $P$-$V$-$T$ relations for MgO in the Mie-Grüneisen-Einstein approach (equations 1 and 5) as a practical high-temperature pressure scales. The equation (1) is formulated within the framework of the Mie-Grüneisen-Einstein model which coincides with the Mie-Grüneisen-Debye model within the limits of high temperatures. The advantage of the $P$-$V$-$T$ relation in the Mie-Grüneisen-Einstein approach as compared with other approaches is the simplicity and analyticity. We have all reasons to assert, that $P$-$V$-$T$ relations calculated from much more complex equations of state can be approximated by the equations (1) and (5) with reasonable accuracy. However, if experimental $P$-$V$-$T$ data are approximated by these equations with physically inadmissible parameters, the reason may be explained by the errors in pressure scales, or the error is related to the nonhydrostatic pressure medium during compression.

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