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# Equations of state for wide ranges in pressure and temperature

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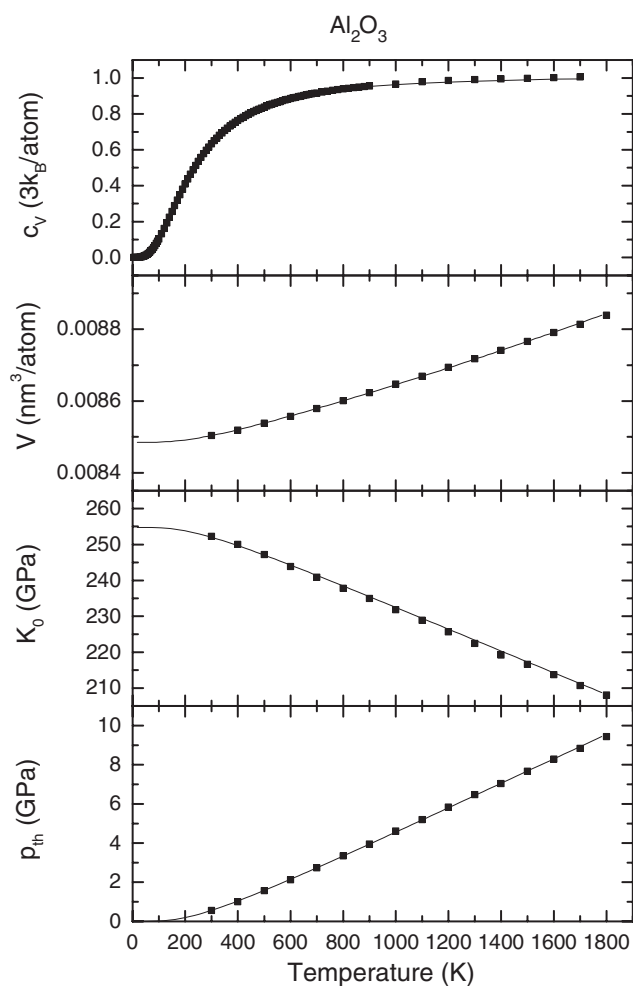
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## Abstract

It has been shown recently (Holzapfel *et al* 2001 *J. Phys. Chem. Ref. Data* **30** 515–29) that equations of state (EOS) data for simple metals like Cu, Ag and Au can be described most accurately on the base of a modified Mie–Grüneisen model including intrinsic anharmonicities. In contrast to commonly applied parametric EOS forms, which use only temperature dependent parameters,  $V(T)$ ,  $K(T)$  and  $K'(T)$ , in the same parametric form, the present approach describes the thermal pressure more accurately and allows therefore to extrapolate more safely into wider ranges of pressure and temperature. Starting from the phonon density of state and a separate modelling of zero temperature and thermal contributions including quasiharmonic and intrinsically anharmonic contributions, the low energy part of the phonon density of states is represented by a modified pseudo-Debye model, which needs only one additional Einstein frequency for the high energy part. This optimised model is successfully applied to describe not only the EOS of Cu, Ag and Au, but also of other simple solids like NaCl and MgO, which are of special interest for pressure measurements in wide ranges of pressure and temperature.

## 1. Introduction

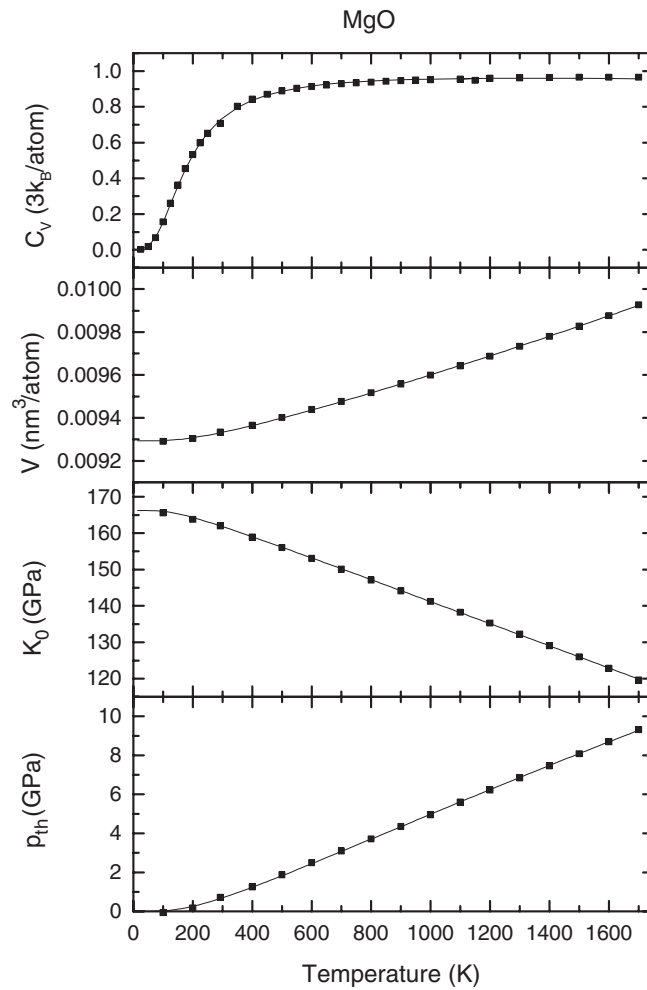
Equations of state (EOS), not only as isothermal  $p(V, T)$  relations near ambient temperature, but also for wide ranges in temperature have become needed more urgently in recent years in many high pressure studies, where the EOS for some simple substances serve as scales for the determination of pressure by means of x-ray diffraction. Due to the lack of an accurate absolute pressure scale for pressures above 5 GPa, a solid theoretical and experimental background for the EOS of many different calibrants can help to reduce the uncertainties in the currently used ‘practical’ pressure scales based primarily on semi-empirical EOS forms with input from ultrasonic measurements at ambient pressure and limited data from shock wave experiments. In the process of linking these data together to generate reliable  $p(V, T)$  EOS for wide ranges in pressure and temperature, some theoretical considerations can help to



**Figure 1.** The specific heat, isothermal bulk modulus, atomic volume and thermal pressure for  $\text{Al}_2\text{O}_3$ . The squares correspond to values calculated from experimental data ( $C_p$  from [16]; all other data from [17]); solid curves correspond to fits using the anharmonic Mie-Grüneisen approach described in the text.

establish a better foundation for optimized EOS forms. This approach uses all the available experimental data at ambient pressure, which include the temperature dependence of the specific volume,  $V_0(T)$ , the thermal expansivity,  $\alpha_0(T)$ , the bulk modulus,  $K_0(T)$ , and the specific heat,  $C_{p0}(T)$ . Experimental high pressure studies with several of these calibrants together under the same pressure and temperature conditions provide then an opportunity to check the internal consistency and probably also the absolute accuracy of these practical pressure scales.

In a first attempt along these lines [1], the EOS for Cu, Ag and Au were determined for wide ranges in pressure and temperature. A comparison with previous EOS data indicated thereby that the previous scales included rather large uncertainties, especially at high temperature. Due to the fact that the EOS formulations for metals include additional uncertainties in the contributions from the conduction electrons, the present study analyses the EOS data of several simple insulating materials, which may be especially useful as pressure reference materials.



**Figure 2.** The specific heat, isothermal bulk modulus, atomic volume and thermal pressure for MgO. The squares correspond to values calculated from experimental data ( $C_p$  from [16]; all other data from [17, 18]; values below 300 K for  $K_S$  from [19]); solid curves correspond to fits using the anharmonic Mie–Grüneisen approach described in the text.

## 2. The Mie–Grüneisen approach

In contrast to parametric EOS forms, which usually present isothermal  $p(V, T)$  relations with temperature dependent parameters ( $V_0(T)$ ,  $K_0(T)$ ,  $K'_0(T)$ ,  $K''_0(T)$ , ...), the Mie–Grüneisen approach [2–7] divides the total pressure

$$p(V, T) = p_g(V) + p_{th}(V, T)$$

into the pressure at zero temperature, the ground state pressure  $p_g(V)$  and an explicit thermal contribution  $p_{th}(V, T)$ . For insulators, the thermal pressure is dominated by the contribution from phonon excitations, represented in the Grüneisen approximation by

$$p_{ph}(V, T) = \gamma_\theta(V) \times 3Nk(\theta(V)/V)u_{ph}(T/\theta).$$

This Grüneisen approach represents all the phonon frequencies by just one characteristic frequency  $\nu_\theta$  or by the corresponding characteristic temperature

$$\theta = h\nu_\theta/k$$

with Planck's  $h$  and Boltzmann's  $k$ . Grüneisen assumed that  $\theta(V)$  depends only on volume and not on temperature at constant volume, and introduced the later called Grüneisen parameter

$$\gamma_\theta = -\partial \ln \theta / \partial \ln V|_T,$$

which shows by definition also only a volume dependence. Most seriously, Grüneisen assumed that the volume dependence of the scaled internal energy  $u_{\text{ph}}(T/\theta)$  is represented perfectly by the volume dependence of  $\theta(V)$ , which means that  $u_{\text{ph}}(t)$  depends only on the scaled temperature  $t = T/\theta$  and not explicitly on volume. For accurate representations of EOS data at high temperature, this quasi-harmonic approximation needs extra corrections for additional 'intrinsic' anharmonicities [3–8], for instance by the use of an anharmonic correction of the characteristic temperature in the form

$$\theta_a(V, T) = \theta(V)(1 - A(V)u(T/\theta(V)))$$

with the anharmonicity parameter  $A(V)$  and, as we will see later, with the additional parameter

$$\gamma_A(V) = -d \ln A / d \ln V \neq 0.$$

If one works out the effects of  $A$  and  $\gamma_A$  on all the thermodynamic relations [8], one finds that one has to distinguish between three different Grüneisen parameters,  $\gamma_\theta(V)$ ,  $\gamma_{\text{tb}}(t, V)$  and  $\gamma_{\text{th}}(t, V)$  with

$$\gamma_{\text{tb}}(t, V) = \gamma_\theta(V) - A(V)\gamma_A(V)u(t)$$

and

$$\gamma_{\text{th}}(t, V) = \gamma_\theta(V) - 2A(V)\gamma_A(V)u(t)$$

with the definition of the thermobaric Grüneisen parameter by

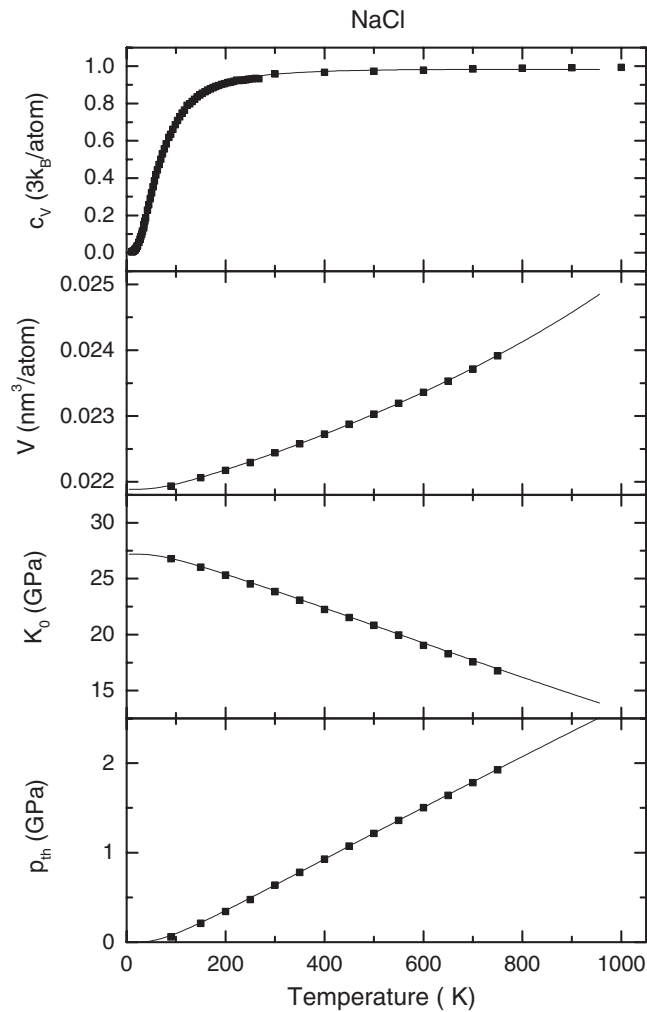
$$\gamma_{\text{tb}}(V, T) = p_{\text{ph}}(V, T)V/U_{\text{ph}}(V, T)$$

and the thermal Grüneisen parameter by

$$\gamma_{\text{th}}(V, T) = \alpha(V, T)VK_T(V, T)/C_V(V, T).$$

With this approach, the ambient pressure data for  $\alpha_0(T)$ ,  $V_0(T)$ ,  $K_{T0}(T)$  and  $C_{V0}(T)$  can be used to determine also  $A$  and  $\gamma_A$  at ambient pressure. These parameters enter into  $\gamma_{\text{tb}}(V, T)$  and thus also into the determination of the thermal pressure [1, 6–10].

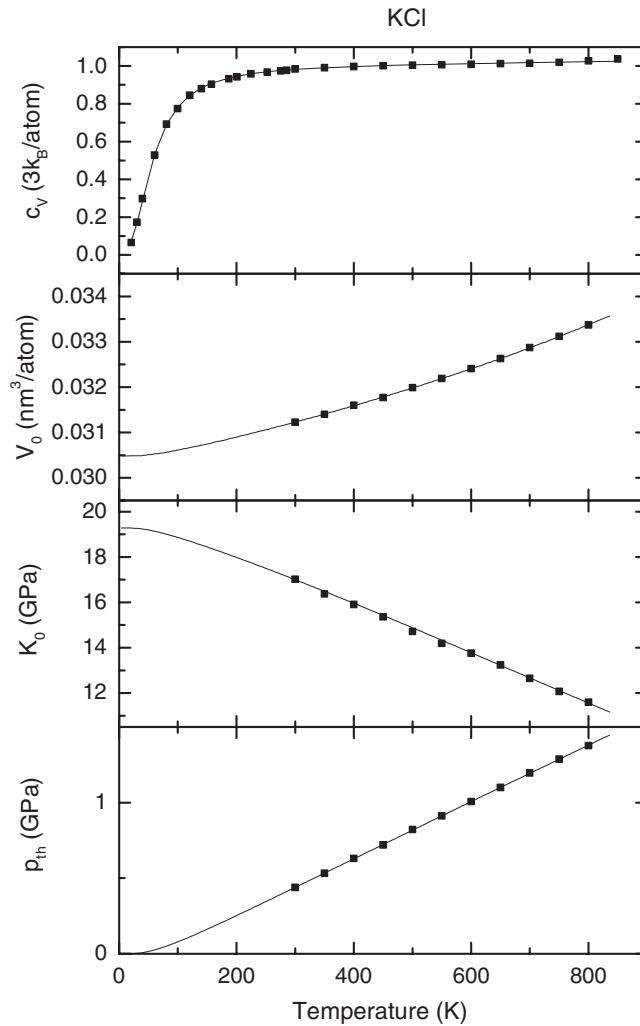
At this point one should notice that the Mie–Grüneisen approach does not yet fix the functional form of the scaled thermal energy  $u(t)$ . Most commonly the Debye model with its rigorous assumptions on the shape of the phonon density of states (DOS) [11] is used to determine the functional form of  $u(t)$ . However, it has been shown that the combination of a mathematically simpler pseudo-Debye form with one (or several) Einstein terms [1, 6–10] gives better results in the representation of all the ambient pressure data. For this reason, an optimized pseudo-Debye–Einstein (opDE) form [10] is also used here for the present evaluation of the EOS data.



**Figure 3.** The specific heat, isothermal bulk modulus, atomic volume and thermal pressure for NaCl. The squares correspond to values calculated from experimental data ( $C_p$  from [16]; all other data from [17]; values below 300 K for  $K_S$  from [19]); solid curves correspond to fits using the anharmonic Mie-Grüneisen approach described in the text.

### 3. The optimized pseudo-Debye-Einstein model

In comparison with the phonon DOS of the Debye model a slightly more realistic representation of the phonon DOS is easily obtained, if one uses two characteristic frequencies or two related temperature parameters. In fact, it is common practice [12] to represent some part of the low frequency phonon DOS by a Debye approximation with the addition of one or several Einstein frequencies for the high frequency part. Computationally it is however more elegant to replace the Debye contribution by a ‘pseudo-Debye’ contribution [13], which corresponds to a bell shaped form of the phonon DOS and represents a much simpler function for the phonon internal energy with the correct  $T$  and  $T^4$  behaviour at high and low temperatures, respectively. In a first attempt along this direction [13], a simple pseudo-Debye (SPD) form



**Figure 4.** The specific heat, isothermal bulk modulus, atomic volume and thermal pressure for KCl. The squares correspond to values calculated from experimental data ( $C_p$  from [16]; all other data from [17]); the solid curves correspond to fits using the anharmonic Mie-Grüneisen approach described in the text.

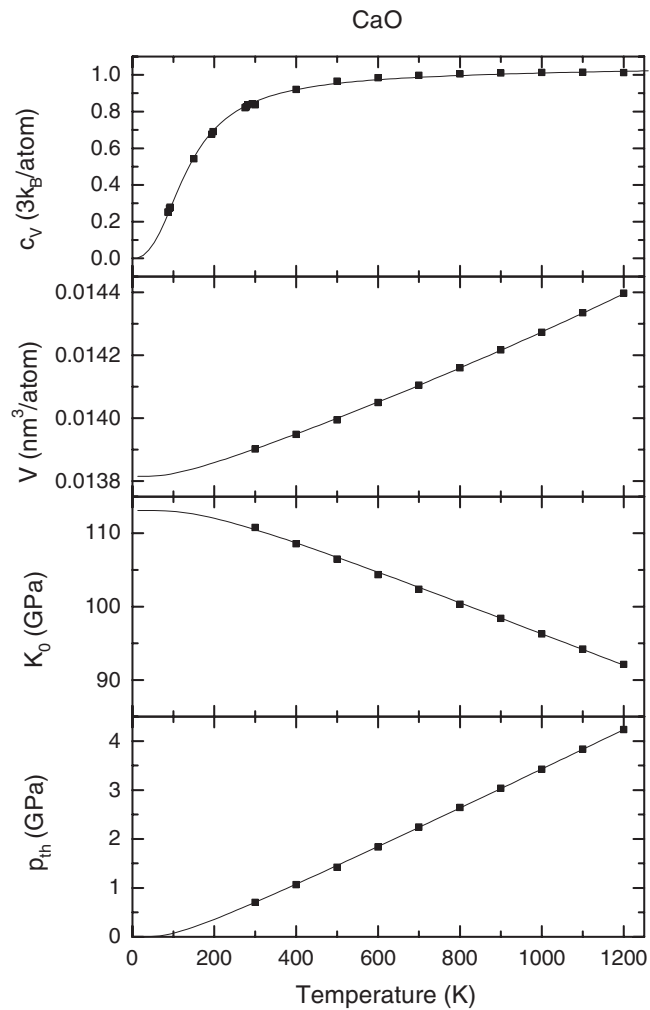
was tested for the normalized internal energy of the phonons  $u_{SPD} = U_{ph}/(3Nk\theta)$  with the normalized temperature  $t = T/\theta$  and neglecting zero-point contributions for the moment:

$$u_{SPD}(t) = t^4/(a + t)^3$$

where  $a = (5/\pi^4)^{1/3} = 0.3716$  results with  $\theta = \theta_{Dacc}$  in a perfect fit of the Debye  $C_{VD}$  at very low temperatures. A better fit of the Debye  $C_{VD}$  over a wide range in temperature is obtained however if one uses a modified pseudo-Debye form,  $u_{MPD}$ , which shows a more favourable behaviour at intermediate temperatures:

$$u_{MPD}(t) = t^4/(a_0 + t^3)$$

and results in an excellent fit of the Debye  $C_{VD}$  when just one additional Einstein term with the frequency ratio  $f = \nu_E/\nu_D = \theta_E/\theta_D$  is used in the corresponding optimized



**Figure 5.** The specific heat, isothermal bulk modulus, atomic volume and thermal pressure for CaO. The squares correspond to values calculated from experimental data ( $C_p$  from [16]; all other data from [17]); the solid curves correspond to fits using the anharmonic Mie–Grüneisen approach described in the text.

pseudo-Debye–Einstein form [10]:

$$u_{\text{opDE}}(t, f) = gt^4/(a_0g + t^3) + (1 - g)f/(e^{f/t} - 1)$$

with the weight of the MPD term  $g = 0.068$  and  $a_0 = 0.0434$ . For the Debye case the frequency ratio  $f$  is constrained in this opDE model to

$$f = (3/4)(1 - g^{4/3})/(1 - g).$$

However, for real solids this ratio is determined by the high temperature limit of the Debye temperature:

$$\theta_{D\infty} = \theta_{\text{Dacc}}(g^{4/3} + (1 - g)f \times 4/3).$$



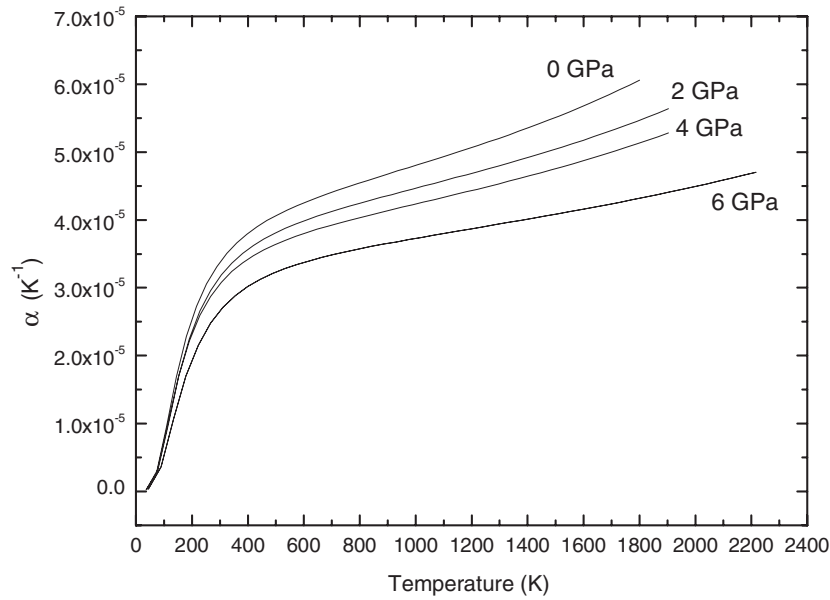


Figure 6. The thermal expansivity for MgO at different pressures and temperatures.

This means that the present opDE model can be applied also to solids with phonon DOS which deviate significantly from the Debye case; and no (artificial) temperature dependence occurs in this quasi-harmonic approximation for the characteristic (Mie–Grüneisen) temperature  $\theta$  within this opDE model.

#### 4. EOS forms for the cold pressure $p_g(V)$

It has been discussed in various places [1, 6–10] that the uncertainties in the extrapolation of common EOS forms can be avoided by the use of an adapted polynomial expansion of the order  $L$ , given by

$$p_{\text{APL}} = 3K_0 x^{-5} (1-x) \exp(c_0(1-x)) \left( 1 + x \sum_2^L c_k (1-x)^{k-1} \right).$$

In this form the parameter  $c_0$  is constrained to the value  $c_0 = -\ln(3K_0/p_{\text{FG0}})$ , where  $p_{\text{FG0}} = a_{\text{FG}}(Z/V_0)^{5/3}$  represents the pressure of a Fermi gas with the total electron number  $Z$  in the (atomic) volume  $V_0$ , and  $a_{\text{FG}} = 0.023\,37 \text{ GPa nm}^5$  is a universal constant for the Fermi gas. Typically, the second-order form AP2 with

$$c_2 = (3/2)(K'_0 - 3) - c_0$$

fits the EOS data for regular solids perfectly with very small values of  $c_2$  for simple AB compounds [14]. If one uses however the third-order form AP3 with the additional parameter  $c_3$ , one can also fit the cohesive energy  $E_0$ .

#### 5. The software for the calculation and fitting of the EOS data

The present program [15] is based on the intention to calculate not only the EOS data but also all the thermophysical properties via a state-of-the-art representation of the free energy

$F(V, T, N)$  (as a thermodynamic potential of the system) with a minimum number of free parameters. This approach needs the following parameters for insulators:

I	For the energy and pressure of the ground state	
I.1	The cohesive energy contribution	: $E_0$
I.2	The equilibrium volume per atom (or cell)	: $V_0$
I.3	The corresponding bulk modulus	: $K_0$
I.4	Its pressure derivative	: $K'_0$
I.5	The number of electrons per atom (or cell)	: $Z$
II	For the phonon contributions	
II.1	The acoustic Debye temperature	: $\theta_{\text{Dacc}} = \theta$
II.2	The Grüneisen parameter of $\theta_{\text{Dacc}}$	: $\gamma_\theta$
II.3	For $\theta_{\text{D}\infty}/\theta_{\text{Dacc}}$ a frequency ratio	: $f$
II.4	The explicit anharmonicity parameter	: $A$
II.5	The Grüneisen parameter of $A$	: $\gamma_A$

**Table 1.** Refined parameters for MgO, CaO, NaCl, KCl and Al<sub>2</sub>O<sub>3</sub> from the TEOSfit program.

$T_r = 300$ K	MgO	CaO	NaCl	KCl	Al <sub>2</sub> O <sub>3</sub>
$Z$	20	28	28	36	50
$V_0(T_r)$ per atom (nm <sup>-3</sup> )	0.009 333	0.013 90	0.022 44	0.031 23	0.008 504
$K_0(T_r)$ (GPa)	162	110.5	23.9	17	252
$K'_0(T_r)$	4.1	4.8	5.4	5.5	5.0
$\theta$ (K)	777	464	277	189	842
$f$	0.821	0.663	0.798	0.938	0.845
$\gamma_0$ ( $\Gamma_0$ Barton–Stacey)	1.44	1.21	1.56	1.38	1.29
$\gamma_0$ ( $\Gamma_0$ free form)	1.54	1.29	1.61	1.40	1.32
$\Gamma_0$ (Barton–Stacey)	0.508	0.309	0.432	0.35	0.3
$\Gamma_0$ (free fit)	1.434	1.154	0.883	0.97	0.713
$A$	$-6.9 \times 10^{-3}$	$8.5 \times 10^{-3}$	$-1.9 \times 10^{-3}$	$2.78 \times 10^{-3}$	$2.27 \times 10^{-3}$
$\gamma_A A$ ( $\Gamma_0$ Barton–Stacey)	-0.190	-0.041 2	-0.0605	-0.008 03	-0.014 59
$\gamma_A A$ ( $\Gamma_0$ free fit)	0.032 4	-0.000 61	0.0157	0.009 86	0.016 30

The present software includes two programs:

- (i) The program TEOSfit determines the phonon parameters (II.1–II.5) in correlated fits of the atomic volume  $V_0(T)$ , the thermal expansion  $\alpha_0(T)$ , the specific heat  $C_{p_0}(T)$  and the adiabatic bulk modulus  $K_{S_0}(T)$  at ambient pressure as input data.
- (ii) The program TEOScalc uses the refined parameters from TEOSfit together with the parameters for one isotherm (I.1–I.5) for the reference temperature  $T_r$  (=300 K) to calculate all the thermodynamic functions, e.g. the  $p(V, T)$  for any pressure and temperature, whereby the reasonable range is constrained to temperatures below the melting curve.

Results of TEOSfit for MgO, CaO, NaCl, KCl and Al<sub>2</sub>O<sub>3</sub> are shown in figures 1–5 and the refined parameters are given in table 1. Since the contribution of the thermal pressure to the total pressure for a series of isotherms does not show up clearly in one figure, figure 6 shows an example of the calculation of the thermal expansivity for MgO. This example illustrates that the thermal expansivity decreases strongly with pressure and the classical range is widened with respect to the quantum regime. A detailed comparison with previous data for the high temperature behaviour of MgO and NaCl is in progress.

## 6. Conclusion

The explicit anharmonic contributions for the present simple insulating materials are very small in comparison with those for the previously studied rare gas solids [9]. From this point of view, the EOS of the present materials do not encounter large uncertainties in their extrapolations to high temperature and are therefore very useful for pressure determinations at high temperature. We found that the values  $K'_0$ ,  $\gamma_0$ ,  $\Gamma_0$  and  $\gamma_A$  are strongly correlated. When the values for  $K'_0$  are taken from the literature [13, 20–22] the Barton–Stacey form does not always lead necessarily to best fits. For all materials in the present paper the use of the fixed Barton–Stacey form for  $\Gamma_0$  produces rather large values for  $\gamma_A A$ . A free form of  $\Gamma_0$  always gives better results. One may notice that even the Mie–Grüneisen case  $A\gamma_A = 0$ , in combination with a free fit of  $\Gamma_0$ , leads to better results than the fixed Barton–Stacey form for  $\Gamma_0$ .

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