

EQUATIONS OF STATE OF CARBONATES FOR THE EARTH'S MANTLE CONDITIONS

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In the last few decades a set of equations of state for solids which can be successfully applied to the description of thermodynamic properties of minerals in wide range of temperatures and pressures have been developed. In the most known work [1] the Debye approach are used for description of quasi-harmonic part of the Helmholtz free energy and additional contributions to the Helmholtz free energy are taken into account. However, the Debye approach is true within the limits of low and high temperatures but in the intermediate field it is interpolar. Oxides and minerals have usually a high the Debye temperature (about 500-1000 K), therefore at room temperatures the Debye approximation is not always correct. For very good description of thermodynamic functions of solids from 10 K up to melting temperature it is possible to used the Bose-Einstein approximation [2, 3] which has been successfully used at construction of equation of state for NaCl [4] and some metals [5, 6]. However in the latter case construction of equations of state needs practically full set of experimental measurements (heat capacity, thermal expansion coefficient, adiabatic bulk modulus from ~ 0 K and up to melting temperature, volume depending on pressure and temperature and shock data) which in most cases are absent for minerals. Other approximations which are quite successfully applied to equations of state for solids are also known (see, for example, [7, 8, 9, 10, 11]). In this work quasiharmonic part of the Helmholtz free energy will be represented by the Agoshkov model [12] using equation of state for magnesite, as example.

Following [1], we'll report the Helmholtz free energy $F(V, T)$ as the sum:

$$F(V, T) = U_0 + E(V) + F_{qh}(V, T) + F_{anh}(V, T), \quad (1)$$

where U_0 is the reference energy, $E(V)$ is the potential (cold) part of the free energy on the reference isotherm, which depends only on volume; $F_{qh}(V, T)$, $F_{anh}(V, T)$ are quasiharmonic part of the Helmholtz free energy, and terms describing intrinsic anharmonicity.

Cold energy is written as [13]:

$$E(V) = 9K_0V_0\eta^{-2} \{1 - [1 - \eta(1 - y)] \exp[(1 - y)\eta]\}, \quad (2),$$

where $y = (V/V_0)^{1/3} = x^{1/3}$ and $\eta = 1.5(K' - 1)$.

For approximation of the quasiharmonic phonon part of the Helmholtz free energy we use the sum:

$$F_{qh}(V, T) = m_D F\left(\frac{\Theta_D}{T}\right) + m_{E1} E_1\left(\frac{\Theta_{E1}}{T}\right) + m_{E2} E_2\left(\frac{\Theta_{E2}}{T}\right), \quad (3)$$

where $m_D + m_{E1} + m_{E2} = 3n$ and n are equal to number of atoms in chemical formula,

$F\left(\frac{\Theta_D}{T}\right) = R \left[\ln(1 - e^{-\Theta_D/T}) - \frac{1}{3} D\left(\frac{\Theta_D}{T}\right) \right]$ is a free energy in the Debye approach,

where $D\left(\frac{\Theta}{T}\right) = \frac{3T^3}{\Theta^3} \int_0^{\Theta/T} \frac{y^3 dy}{e^y - 1}$ is the Debye function, $E_1\left(\frac{\Theta_{E1}}{T}\right) = RT \ln(1 - e^{-\Theta_{E1}/T})$

and $E_2\left(\frac{\Theta_{E2}}{T}\right) = RT \ln(1 - e^{-\Theta_{E2}/T})$ are free energy in the Einstein approach, R is gas constant.

Comparing (3) with equations for heat capacity and entropy with [12], we see that they properly coincide, but in our case the model [12] is extended on the Helmholtz free energy. In contrast to Agoshkov [12], we shall find characteristic temperatures Θ and parameters m from low temperature measurements of heat capacity which are known for many minerals, included those of complicated composition, though as well as in [12] they may be determined from phonon spectrum of crystal lattice. For simplification of calculations the Debye function can be approximated by analytical expressions, for example, [14], [15]. In the equation (3) and below Θ is characteristic temperature which depend on volume. Volume dependence of Θ (or from compression $x = V/V_0$) for all contributions are given as [16]:

$$\Theta = \Theta_0 x^{-\gamma_\infty} \exp\left[\frac{\gamma_0 - \gamma_\infty}{\beta} (1 - x^\beta)\right], \quad (4),$$

where γ_0 is the Grüneisen parameter at ambient conditions, γ_∞ is the Grüneisen parameter at $x=0$ and β is fitting parameter. For minerals we used approximation $\beta = \gamma_0 / (\gamma_0 - \gamma_\infty)$.

The intrinsic anharmonicity contribution to the Helmholtz free energy at temperature > 100 K is taken as [1]:

$$F_{anh}(V, T) = -\frac{3}{2} n R a T^2 = -\frac{3}{2} n R a_0 x^m T^2.$$

Differentiating (1), we obtain all the necessary thermodynamic functions: entropy, $S = -(\partial F / \partial T)_V$, internal energy $E = F + TS$, heat capacity at constant volume, $C_V = (\partial E / \partial T)_V$, pressure, $P = -(\partial F / \partial V)_T$, isothermal bulk modulus, $K_T = -V(\partial P / \partial V)_T$, slope of pressure at constant volume $(\partial P / \partial T)_V = \alpha K_T$, where $\alpha = 1/V(\partial V / \partial T)_P$. Heat capacity at constant pressure is $C_P = C_V + \alpha^2 T V K_T$, adiabatic bulk modulus is $K_S = K_T + V T (\alpha K_T)^2 / C_V$. The enthalpy and Gibbs energy can be found from $H = E + PV$, $G = F + PV$.

Below fig. 1 shows results of simultaneous processing of heat capacity [17] of magnesite in comparison with reference [18], [19] and previous data [20], thermal expansion coefficient [21] in comparison with other estimations [20], [22], and also bulk moduli from ultrasonic [23], [24] data and their calculation from PVT measurements [22].

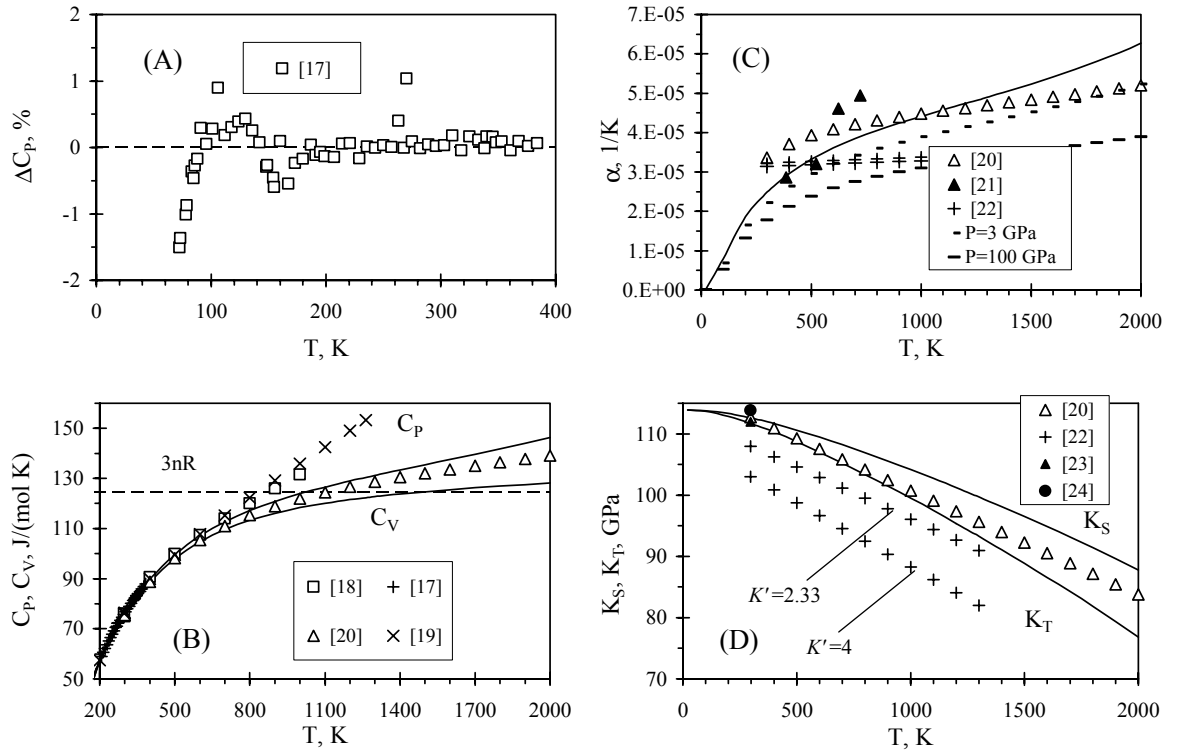


Fig.1. Comparison of measured low-temperature (A) and high-temperature (B) heat capacity of magnesite with our calculation and other data, thermal expansion coefficient (C) and bulk moduli (D).

The obtained equation of state for magnesite has the following parameters: $V_0=28.016$ cm³, $K_0=111.7$ GPa, $K'=4.06$, $m_D=7.183$, $\Theta_D=484$ K, $m_{E1}=4.349$, $\Theta_{E1}=1698$ K, $m_{E2}=3.468$, $\Theta_{E2}=734$ K, $\gamma_0=1.029$, $\gamma_\infty=0.75$, $a_0=-20 \cdot 10^{-6}$ K, $m=1.5$. C_P , α and bulk moduli calculated from this equation quite well agree with estimations of thermodynamic functions of the magnesite, obtained from oscillatory spectra [20].

PVT relations for magnesite are measured up to pressure 120 GPa [25–29] at room temperature and up to 8.6 GPa and 1285 K [22], and Hugoniot curve as well [30]. These measurements and [32] are compared with our calculation in fig. 2 and calculation from the first principles [31].

Thus, we have constructed wide range equation of state for magnesite on the basis of Agoshkov [12] model which is well consistent with experimental measurements in a range of temperatures from 100 K and up to pressure 120 GPa, with shock data and theoretical calculations.

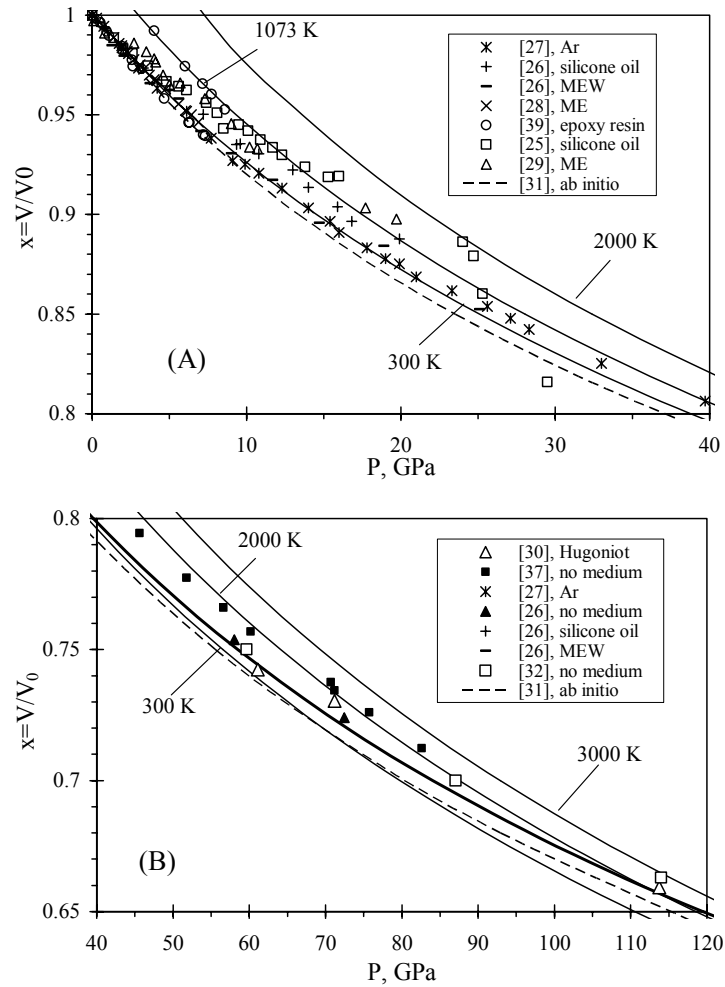


Fig.2. Calculated isotherms of magnesite in the range of 0-40 GPa (A) and 40-120 GPa (B). A bold line is the calculated Hugoniot curve.

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