Semiempirical pressure-volume-temperature equation of state: MgSiO$_3$ perovskite is an example

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Simple general formula describing the pressure-volume-temperature relationships (*p-V-T*) of elastic solids is constructed from theoretical considerations. The semiempirical equation of state (EOS) was tested to experiments of perovskite 0–109 GPa and 293–2000 K. The parameters providing the best fit are $B_0 = 267.5$ GPa, $V_0 = 24.284$ cm^3, $\alpha_0 = 2.079 \times 10^{-5}$ K^{-1}, $\partial B_0 / \partial p = 1.556$, and $\partial \alpha_0 / \partial p = -1.098 \times 10^{-7}$ K^{-1} GPa^{-1}. The root-mean-square deviations (RMSDs) of the residuals are 0.043 cm^3, 0.79 GPa, and 125 K for the molar volume, pressure, and temperature, respectively. These RMSD values are in the range of the uncertainty of the experiments, indicating that the five-parameter semiempirical EOS correctly describes the *p-V-T* relationships of perovskite. Separating the experiments into 200 K ranges the semiempirical EOS was compared to the most widely used finite strain, interatomic potential, and empirical isothermal EOSs such as the Birch-Murnaghan, the Vinet, and the Roy-Roy, respectively. Correlation coefficients, RMSDs of the residuals, and Akaike Information Criteria were used for evaluating the fitting. Based on these fitting parameters under pure isothermal conditions the semiempirical *p-V* EOS is slightly weaker than the Birch-Murnaghan and Vinet EOSs; however, the semiempirical *p-V-T* EOS is superior in every temperature range to all of the investigated conventional isothermal EOSs. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2822458]

I. INTRODUCTION

The relationships among the pressure, the volume, and the temperature are described by the equation of state (EOS). The basic relationship between the volume and the temperature is described by the definition of the volume coefficient of expansion, α_V, as follows:

$$\alpha_{V_p} \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p. \tag{1}$$

The relationship between the pressure and the volume is given by the isothermal bulk modulus, B_T, as follows:

$$B_T \equiv -V\left(\frac{\partial p}{\partial V}\right)_T. \tag{2}$$

For the validity of Eq. (2) it is assumed that the solid is homogeneous, isotropic, nonviscous, and has linear elasticity. It is also assumed that the stresses are isotropic; therefore, the principal stresses can be identified as the pressure $p = \sigma_1 = \sigma_2 = \sigma_3$.

Experiments show that both the volume coefficient of expansion and the isothermal bulk modulus are pressure and temperature dependent; therefore, it is necessary to know the derivatives of these parameters.

$$\left(\frac{\partial \alpha_V}{\partial T}\right)_p, \quad \left(\frac{\partial \alpha_V}{\partial p}\right)_T, \quad \left(\frac{\partial B_T}{\partial T}\right)_p, \quad \left(\frac{\partial B_T}{\partial p}\right)_T. \tag{3}$$

The schematic relationships between the thermodynamic quantities and parameters are shown in Fig. 1(a). A universal EOS must cover the entire pressure and temperature range; therefore, it is necessary to incorporate all of the derivatives

of the volume coefficient of expansion and the isothermal bulk modulus. The EOS is an integral part of the Helmholtz and Gibbs free energies and an important tool describing the pressure-temperature-composition relationships.[1] There is no single expression known for universal (*p-V-T*) EOS.[2,3]

II. DESCRIBING THE *P-V-T* RELATIONSHIP

In order to overcome the complexity of the EOS, the common practice is that the temperature of the substance is raised first and then the substance is compressed along the isotherm of interest.[4,5] The relevant equations are called the thermal and isothermal EOSs, respectively. The thermal EOS is used to calculate the volume at atmospheric pressure and temperature T, $V_{0,T}$. It is also necessary to know the temperature effect on the bulk modulus, $B_0(T)$. Using the values of the volume and the bulk modulus at the corresponding temperature the isothermal EOS calculates the effect of pressure by incorporating the first and second derivates of the bulk modulus, $(\partial B / \partial p)_T$ and $(\partial^2 B / \partial p^2)_T$, at the given temperature.

A. Thermal EOS

The simplest thermal equation of state is derived by the integration of the thermodynamic definition of the volume coefficient of thermal expansion [Eq. (1)],

$$V_0(T) = V_0(T_0)e^{\int_{T_0}^{T}\alpha_{V_p}(T)dT}. \tag{4}$$

If a wider temperature range is considered then the temperature dependence of the volume coefficient of thermal expansion should be known. Knowing the first derivative of this parameter allows one to calculate the high temperature values as follows:

(a.)   Solid phase   **(b.)**
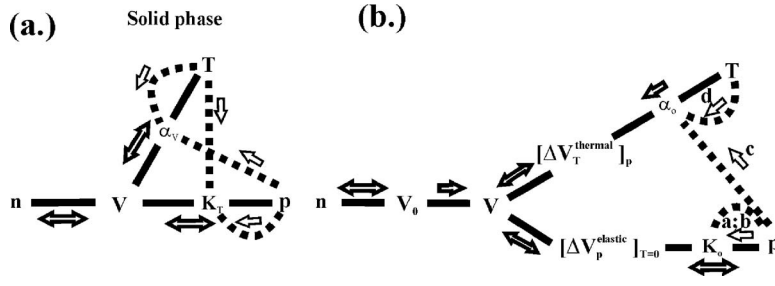
$$\alpha_{V_p}(T) = \alpha_{V_p}(T_0) + \left(\frac{\partial \alpha_V}{\partial T}\right)_p (T - T_0). \tag{5}$$

The thermodynamic Gruneisen-Anderson parameter, δ_T, is defined as[6]

$$\delta_T = \left(\frac{\partial \ln B_T}{\partial \ln \rho}\right)_p = -\frac{1}{\alpha_V}\left(\frac{\partial \ln B_T}{\partial T}\right)_p. \tag{6}$$

Assuming that the solid at higher temperatures follows classical behavior, then the product of $\alpha_{V_p} B_T$ is constant and the Gruneisen-Anderson parameter is independent of temperature. Anderson et al.[7] and Shanker and Kumar[8] proposed the following isobaric EOS:

$$V = V_0[1 - \alpha_{V_0}\delta_0(T - T_0)]^{-1/\delta_0}, \tag{7}$$

where the subscript zero values of the parameters refers to the initial temperature of T_0.

Assuming that the product of $\alpha_{V_p} B_T$ is constant and the Gruneisen-Anderson parameter changes linearly with the volume, the following EOS has been proposed by Kumar[9] and Kushwah et al.:[10]

$$V = V_0\left\{1 - \frac{1}{A}\ln[1 - \alpha_{V_0}A(T - T_0)]\right\}, \tag{8}$$

where $A = \delta_0 + 1$.

Thermal EOSs have been suggested by Akaogi and Navrotsky,[11,12] assuming that the thermal expansion is quadratic in temperature and independent of pressure,

$$V_p = V_0[1 + \alpha_{V_0}(T - T_0) + \alpha'_{V_0}(T - T_0)^2], \tag{9}$$

where α'_{V_0} is the temperature derivative of α_V at temperature $T = T_0$. Taking into consideration the effect of pressure the equation can be written as

$$V_{p,T} = V_0\left[1 + \frac{B'_0(p - p_0)}{B_0}\right]^{-1/K'_0}[1 + \alpha_{V_0}(T - T_0) + \alpha'_{V_0}(T - T_0)^2]. \tag{10}$$

Fei and Saxena[13] revised the quadratic relationship of Eq. (10) and proposed the following empirical expression:

$$V_p = V_0\left[1 + \alpha_{V_0}(T - T_0) + \tfrac{1}{2}\alpha'_{V_0}(T - T_0)^2 - \alpha_{V_0}(T - T_0)^{-1}\right]. \tag{11}$$

Assuming linear change as a function of temperature in the volume coefficient of thermal expansion leads to the following expression:[14]

$$V_p = V_0 e^{\alpha(T - T_0) + (1/2)\alpha'(T - T_0)^2}. \tag{12}$$

The proposed general expression of Eq. (12) for bcc iron is

$$V_p = V_0\left\{1 + B'_0\left[B_0 - \left(\frac{\partial B}{\partial T}\right)_0 (T - T_0)\right]\frac{p - p_0}{B_0^2}\right\}^{-1/K'_0}$$
$$\times e^{\alpha(T - T_0) + (1/2)\alpha'(T - T_0)^2}. \tag{13}$$

An empirical expression has been given by Plymate and Stout,[15]

$$V = V_0\left\{\left[1 + \left(\frac{\partial B_T}{\partial T}\right)_0\left(\frac{T - T_0}{B_0}\right)\right]^{-1/B'_0}\right.$$
$$\left.\times e^{[\alpha_{V_0} + (\partial B_T/\partial T)_0 1/B_0 B'_0](T - T_0) + [\alpha'_{V_0} + (\partial B_T/\partial T)_0^2 1/B_0^2 B'_0](T - T_0)^2/2}\right\}. \tag{14}$$

B. The temperature effect on the bulk modulus

The effect of the temperature on the bulk modulus is discussed in detail in Ref. 16 Assuming constant value for the product of the volume coefficient thermal expansion and the bulk modulus allows deriving an analytical solution for the temperature dependence of the bulk modulus at temperatures higher than the Debye temperature.[16]

$$B_T = e^{-\int_{T=0}^{T}\delta_T \alpha_V dT} B_{T=0}, \tag{15}$$

where δ_T is the isothermal Anderson-Gruneisen parameter given by

$$\delta_T = -\frac{1}{\alpha_{V_p} B_T}\left(\frac{\partial B_T}{\partial T}\right)_p. \tag{16}$$

C. Isothermal EOS

The determined values of the volume and the bulk modulus at temperature T can be used as initial parameters for an isothermal EOS. The isothermal equations of states follow finite strain, interatomic potential, or empirical approach.

1. Finite-strain EOS

The Birch-Murnaghan EOS (Refs. 17–19) assumes that the strain energy of a solid can be expressed as a Taylor series in the finite Eulerian strain, f_E. Expansion to fourth order in the strain yields an EOS,

$$p = 3B_0 f_E(1 + 2f_E)^{5/2}\left\{1 + \tfrac{3}{2}(B' - 4)f_E\right.$$
$$\left. + \tfrac{3}{2}\left[B_0 B'' + (B' - 4)(B' - 3) + \tfrac{35}{9}\right]f_E^2\right\}, \tag{17}$$

where f_E is

$$f_E = \frac{\left(\frac{V_0}{V}\right)^{2/3} - 1}{2}.$$ (18)

The most widely used isothermal EOS is the third-order Birch-Murnaghan. Quite recently Sushil et al.[20] used $n=1$ instead of the $n=2$ in the Eulerian strain measure

$$f_E = \frac{\left(\frac{V_0}{V}\right)^{n/3} - 1}{n} = \left(\frac{V_0}{V}\right)^{1/3} - 1$$ (19)

and using the method of Stacey[21] proposed a modified three-parameter Eulerian strain EOS,

$$p = \frac{9}{2}B_0(-A_1 x^{-4/3} + A_2 x^{-5/3} - A_3 x^{-2} + A_4 x^{-7/3}),$$ (20)

where

$$x = \frac{V}{V_0}, \quad A_1 = B_0 B_0'' + (B_0' - 3)^2 + \frac{26}{9},$$

$$A_2 = 3B_0 B_0'' + (B_0' - 3)(3B_0' - 8) + \frac{66}{9},$$

$$A_3 = 3B_0 B_0'' + (B_0' - 3)(3B_0' - 7) + \frac{60}{9},$$

and

$$A_4 = B_0 B_0'' + (B_0' - 3)(B_0' - 2) + \frac{20}{9}.$$

The authors claimed that their modified Eulerian strain EOS is more rapidly convergent than the Birch-Murnaghan EOS.

2. Interatomic potential EOSs

The theoretical base for the interatomic potential EOS lays in the thermodynamic relationship

$$p = T\left(\frac{\partial p}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_{T,m},$$ (21)

where m stands for a mol quantity. Neglecting the thermal pressure[22,23] and approaching the second term, the so-called internal pressure, with the volume derivative of the binding energy, allow determining the pressure-volume relationship. The resulting EOS contains three parameters, the zero pressure values of the molar volume, the isothermal bulk modulus, and the pressure derivative of the bulk modulus.

Using the potential function proposed by Mie and extended by Gruneisen[24,25]

$$U(r) = -\frac{A}{r^m} - \frac{B}{r^n} = -\frac{A}{V^{(m/3)}} + \frac{B}{V^{(n/3)}},$$ (22)

where r is the interatomic spacing and A, B, m, and n are constants (not necessarily integers) the p-V equation of state can be written as[26]

$$p = \frac{3B_T(0)}{m-n}\left\{\left(\frac{V_0}{V}\right)^{[(m+3)/3]} - \left(\frac{V_0}{V}\right)^{[(n+3)/3]}\right\}.$$ (23)

The so-called universal EOS derived by Rose et al. from a general interatomic potential,[27] which was promoted by Vinet et al.,[22,23] is also commonly used,

$$p = 3B_0\frac{1-f_V}{f_V^2}e^{[3/2(B'-1)(1-f_V)]},$$ (24)

where

$$f_V = \left(\frac{V}{V_0}\right)^{1/3}.$$ (25)

The Vinet EOS gives very accurate results for simple solids at very high pressure.

Some authors[28,29] pointed out that there is a restriction on Eq. (24) when it is applied to high-pressure phase solids under low-pressure conditions. The use of $p=0$ and $V=V_0$ is sometimes arbitrary since the high-pressure phase might not exist under this condition. In order to overcome on this problem Fang[30] suggested modifying the original Vinet equation (24) by introducing an additional parameter. In this modified equation it was assumed that the isothermal bulk modulus varies linearly with the pressure.

Precise knowledge of the interatomic forces in the stress-free state and their variation with pressure and temperature would allow calculating all the thermodynamic properties. The lack of such knowledge has resulted in many two- and three-parameter empirical EOSs.

3. Empirical EOSs

Empirical EOSs can be divided into two major groups. One uses the original Eulerian strain or interatomic potential EOSs and refines their parameters in order to find a better fit to experiments.[31–34] The other approach is to find a mathematical function which gives the best fit to the experiments.[35–38]

Roy and Roy[39] gave a good review and evaluate the fittings of the currently used EOSs. Their proposed[40] three-parameter empirical EOS is

$$V = V_0\left[1 - \frac{\ln(1+ap)}{b+cp}\right],$$ (26)

where

$$a = \frac{1}{8B_0}[3(B_0'+1) + (25B_0'^2 + 18B_0' - 32B_0 B_0'' - 7)^{1/2}],$$

$$b = \frac{1}{8}[3(B_0'+1) + (25B_0'^2 + 18B_0' - 32B_0 B_0'' - 7)^{1/2}],$$

$$c = \frac{1}{16}[3(B_0'+1) + (25B_0'^2 + 18B_0' - 32B_0 B_0'' - 7)^{1/2}]\left[(B_0'\right.$$

$$\left. + 1) - \frac{1}{8}[3(B_0'+1) + (25B_0'^2 + 18B_0' - 32B_0 B_0''\right.$$
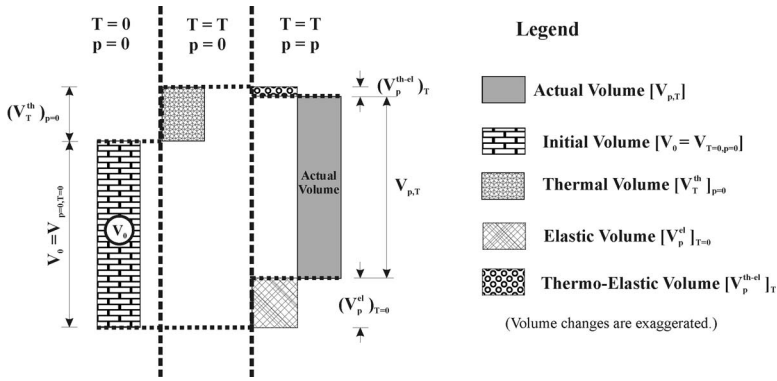
$$\left. - 7)^{1/2}]\right].$$

FIG. 2. The fundamental volume components of the actual volume (Eq. (40)).

They used shock compression data of different metals[41] and the calculated EOS of halite[42] to evaluate the proposed equation up to ultrahigh pressures.

The empirical nature of these equations usually leads to a lack of generality and careful inspection reveals that a particular equation typically gives excellent fitting only for special substances or a specially selected pressure and/or temperature range.

Many of the parameters in the EOS are inter-related, which adds to the complexity of calculations. The optimum values of each of the inter-related parameters have to be determined by confidence ellipses.[5,43] The thermodynamic description of solids is complicated, time consuming, labor intensive, and expensive.

III. FUNDAMENTAL COMPONENTS OF THE VOLUME IN SOLID PHASE

Avogadro's principle does not apply to solids contrarily to gases. Matter in solid phase occupies an initial volume, V_0, at zero pressure and temperature.

$$V_0 = nV_0^m, \tag{27}$$

where n is the number of moles and V_0^m is the molar volume of the substance at zero pressure and temperature. The pressure modifies this initial volume by inducing elastic deformation while the temperature by causing thermal deformation. Using Eqs. (1) and (2) the actual volume at given pressure and temperature can be calculated[44] by allowing one of the variables to change while the other one held constant,

$$[V_T]_{p=0} = V_0 e^{\int_{T=0}^{T} \alpha_{V_{p=0}} dT} \quad \text{or} \quad [V_p]_{T=0} = V_0 e^{-\int_{p=0}^{p} (1/B_{T=0}) dp} \tag{28}$$

and then

$$[V_T]_p = [V_p]_{T=0} e^{\int_{T=0}^{T} \alpha_{V_p} dT} \quad \text{or} \quad [V_p]_T$$
$$= [V_T]_{p=0} e^{-\int_{p=0}^{p} (1/B_T) dp}. \tag{29}$$

These two steps might be combined into one and the volume at a given p, and T can be calculated as follows:

$$V_{p,T} = V_0 e^{\int_{T=0}^{T} \alpha_{V_{p=0}} dT - \int_{p=0}^{p} (1/B_T) dp}$$
$$= V_0 e^{\int_{T=0}^{T} \alpha_{V_p} dT - \int_{p=0}^{p} (1/B_{T=0}) dp}. \tag{30}$$

The total volume change related to the temperature will be called thermal volume, V^{th}, while the total volume change

resulted from elastic deformation will be called elastic volume, V^{el}. The thermal volume at zero pressure is

$$[V_T^{\text{th}}]_{p=0} = V_0 (e^{\int_{T=0}^{T} \alpha_V dT} - 1), \tag{31}$$

while the elastic volume at zero temperature is

$$[V_p^{\text{el}}]_{T=0} = V_0 [e^{-\int_{p=0}^{p} (1/B_T) dp} - 1]. \tag{32}$$

The thermal volume at pressure p is

$$[V_T^{\text{th}}]_p = [V_T^{\text{th}}]_{p=0} e^{-\int_{p=0}^{p} (1/B_T) dp}$$
$$= V_0 e^{-\int_{p=0}^{p} (1/B_T) dp} (e^{\int_{T=0}^{T} \alpha_V dT} - 1), \tag{33}$$

and the elastic volume at temperature T is

$$[V_p^{\text{el}}]_T = [V_p^{\text{el}}]_{T=0} e^{\int_{T=0}^{T} \alpha_V dT} = V_0 e^{\int_{T=0}^{T} \alpha_V dT} [e^{-\int_{p=0}^{p} (1/B_T) dp} - 1]. \tag{34}$$

The actual volume is the sum of the volume components as follows:

$$[V_T]_p = V_0 + [V_p^{\text{el}}]_{T=0} + [V_T^{\text{th}}]_p \quad \text{or} \quad [V_p]_T = V_0 + [V_p^{\text{el}}]_T$$
$$+ [V_T^{\text{th}}]_{p=0}. \tag{35}$$

Since

$$[V_T]_p = [V_p]_T, \tag{36}$$

from Eq. (35) it follows that

$$[V_T^{\text{th}}]_p - [V_T^{\text{th}}]_{p=0} = [V_p^{\text{el}}]_T - [V_p^{\text{el}}]_{T=0}. \tag{37}$$

The compressed part of the thermal volume is the same as the expanded part of the elastic volume. Since the volume
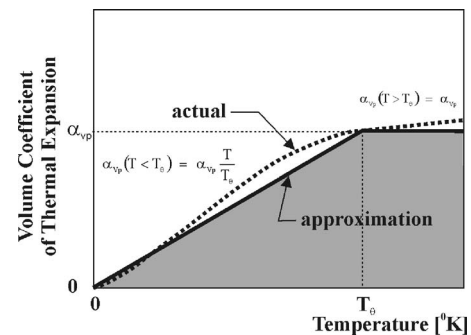

FIG. 3. Approximation used for the volume coefficient of thermal expansion in Eqs. (71) and (73).
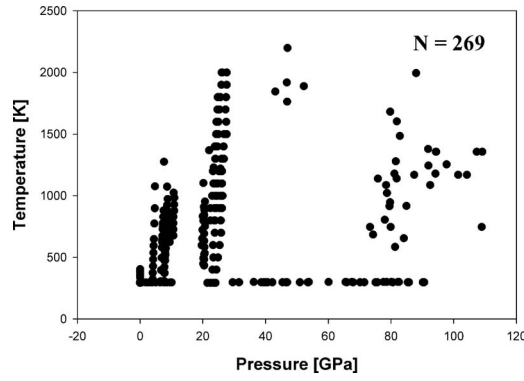
FIG. 4. Pressure-temperature range covered by the experiments of perovskite.

difference in Eq. (37) is both temperature and pressure dependent I will call this volume difference thermoelastic volume $[\Delta V_p^{\text{th-el}}]_T$,

$$[V_p^{\text{th-el}}]_T = [V_T^{\text{th}}]_p - [V_T^{\text{th}}]_{p=0} = [V_p^{\text{el}}]_T - [V_p^{\text{el}}]_{T=0}. \quad (38)$$

The thermoelastic volume can be calculated as

$$[V_p^{\text{th-el}}]_T = V_0(e^{\int_{T=0}^{T}\alpha_V dT} - 1)[e^{-\int_{p=0}^{p}(1/B_T)dp} - 1]. \quad (39)$$

It can be concluded that the actual volume comprises four distinct volume parts: initial volume, thermal volume at zero pressure $[V_T^{\text{th}}]_{p=0}$, elastic volume at zero temperature $[V_p^{\text{el}}]_{T=0}$, and thermoelastic volume $[V_p^{\text{th-el}}]_T$ (Fig. 2).

$$V = V_0 + [V_T^{\text{th}}]_{p=0} + [V_p^{\text{el}}]_{T=0} + [V_p^{\text{th-el}}]_T. \quad (40)$$

These fundamental volume components are related to the thermophysical variables as follows:

$$V_0 = f(n)_{T=0;p=0}, \quad (41)$$

$$[V_T^{\text{th}}]_{p=0} = f(T)_{n;p=0}, \quad (42)$$

$$[V_p^{\text{el}}]_{T=0} = f(p)_{n;T=0}, \quad (43)$$

and

$$[V_p^{\text{th-el}}]_T = f(T,p)_n. \quad (44)$$

It is concluded that the volume changes caused by the temperature and pressure are not equivalent and that Eqs. (1) and (2) do not give a complete description of the volume changes of elastic solids.

The description of the p-V-T relationships of elastic solids requires four equations. The relationship between the initial volume and the number of moles is defined by Eq. (27) as

$$V_0 \equiv nV_0^m \Rightarrow V_0 = f(n)_{T=0;p=0}. \quad (45)$$

The relationship between the elastic volume and the pressure can be defined as

$$B_{T=0} \equiv -(V_0 + V^{\text{el}})\left(\frac{\partial p}{\partial V^{\text{el}}}\right)_{T=0} \Rightarrow V^{\text{el}} = f(p)_{T=0;V_0}. \quad (46)$$

Definition of Eq. (1) can be used to describe the relationship between the temperature and the thermal volume at a given pressure,

$$\alpha_{V_p} \equiv \frac{1}{V_{p,T=0} + V_p^{\text{th}}}\left(\frac{\partial V^{\text{th}}}{\partial T}\right)_p \Rightarrow [V_T^{\text{th}}]_p = f(T)_{p;V_0}. \quad (47)$$

The sum of the fundamental volume components restores the actual volume as

$$V_{p,T} \equiv V_0 + V_p^{\text{el}} + [V_T^{\text{th}}]_p \Rightarrow V_{p,T} = f(V_0; V^{\text{el}}; [V_T^{\text{th}}]_p). \quad (48)$$

The simplest EOS resulting from these four definitions [Eqs. (45)–(48)] is

$$V_{p,T} = nV_0^m e^{\int_{T=0}^{T}\alpha_{V_p}dT - \int_{p=0}^{p}(1/B_{T=0})dp} = nV_0^m e^{\alpha_{V_p}T - (p/B_{T=0})}. \quad (49)$$

IV. THE PROPOSED EOS

By definition [Eq. (46)] the temperature derivative of the bulk modulus is zero. This zero value is also consistent with theory since the interatomic energies are independent of the temperature. Thus the temperature derivatives of this parameter should remain zero at any temperature,

$$\frac{\partial B}{\partial T} = 0. \quad (50)$$

Assuming that the pressure dependence of the bulk modulus can be described by a linear, a, and a quadratic factor, b, results in

$$B = B_0 + ap + bp^2, \quad (51)$$

where

TABLE I. p-V-T fitting parameters and results.

0–109 GPa (N=269)	B_0 (GPa)	V_0 (cm^3)	α_0 (10^{-5} K^{-1})	a	b (10^{-3})	c (10^{-7})	d (10^{-10})	g	R	RMSD	AIC
$V(p,T)$ (S-E-7)	272.5	24.287	1.961	1.384	1.427	−1.081	6.140		0.999 604 88	0.042	−1687.2
$V(p,T)$ (S-E-6)	271.5	24.278	2.075	1.426	1.078	−1.120			0.999 603 60	0.042	−1688.4
$V(p,T)$ (S-E-5)	267.5	24.284	2.079	1.556		−1.098			0.999 600 89	0.043	−1688.5
$V(p,T)$ (Debye)	265.69	24.460	2.610	1.507		−1.510			0.999 387 00	0.053	−1573.1
$V(p,T)$ (Debye+pres)	264.56	24.463	2.489	1.487		−1.592		−6.499	0.999 438 65	0.051	−1594.8
$p(V,T)$ (S-E-5)										0.792	−125.6
$T(V,p)$ (S-E-5)										125.0	2597.8

$$B_0 \equiv \lim_{p \Rightarrow 0} B_{T=0}. \tag{52}$$

Using Eq. (12) and substituting $0.5\alpha'$ with a constant multiplier, d, the temperature dependence of the volume coefficient of thermal expansion at zero pressure can be described as

$$\alpha_{V_{p=0}} = \alpha_0 + dT, \tag{53}$$

where

$$\alpha_0 \equiv \lim_{T \Rightarrow 0} \alpha_{V_{p=0}}. \tag{54}$$

The thermal volume at a given pressure comprises the thermal volume at zero pressure and the thermal elastic volume [Eq. (38)]. In order to take into account the effect of pressure on the thermal volume a constant pressure derivative, c, is inroduced as follows:

$$\alpha_{p,T=0} = \alpha_0 + cp. \tag{55}$$

It is also assumed that the temperature factor, d, in Eq. (53) changes in the same rate as $\alpha_{p,T=0}$ as a function of pressure. Introducing a normalizing pressure factor from Eq. (55),

$$\left(1 + \frac{cp}{\alpha_0}\right) \tag{56}$$

gives the pressure and temperature dependence of the volume coefficient of thermal expansion

$$\alpha_{T,p} = \alpha_{p,T=0} + \left(1 + \frac{cp}{\alpha_0}\right)dT. \tag{57}$$

Substituting Eq. (55) into Eq. (57) results in

$$\alpha_{T,p} = \alpha_0 + cp + \left(1 + \frac{cp}{\alpha_0}\right)dT = \left(1 + \frac{cp}{\alpha_0}\right)(\alpha_0 + dT). \tag{58}$$

Combining Eqs. (49), (51), and (57) gives the p-V-T relationship for elastic solids as

$$V = nV_0^m e^{-p/(ap+bp^2+B_0)+(1+cp/\alpha_0)(\alpha_0+dT)T} \quad \text{(S-E-7)}. \tag{59}$$

Equation (59) contains seven parameters: V_0^m, K_0, α_0, a, b, c,

and d; and will be labeled as Semiempirical 7 (S-E-7). The thermodynamic relationships incorporated into Eq. (59) are shown in Fig. 1(b). Equation (59) has an analytical solution for the temperature,

$$T = \frac{-\alpha_0 \pm \sqrt{\alpha_0^2 + 4d\dfrac{\ln\left(\dfrac{V}{V_0}\right) + \dfrac{p}{ap+bp^2+B_0}}{1+\dfrac{cp}{\alpha_0}}}}{2d}. \tag{60}$$

The pressure can be determined by repeated substitutions as

$$p = \lim_{n \to \infty} f^n(p), \tag{61}$$

where
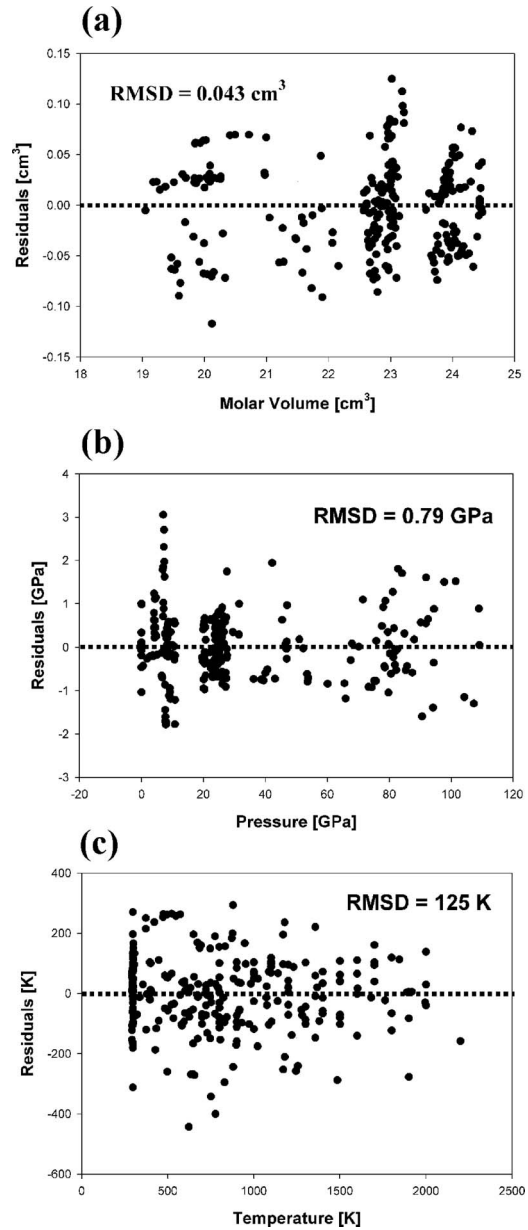
FIG. 5. The residuals plotted against (a), volume, (b) pressure and (c) temperature.

$$f^n(p) = (B_0 + ap_{n-1} + bp_{n-1}^2)\left[\left(1 + \frac{cp_{n-1}}{\alpha_0}\right)(\alpha_0 + dT)T - \ln\left(\frac{V}{V_0}\right)\right], \quad n \in \mathbb{N}^* \tag{62}$$

and

$$p_0 = 0.$$

The convergence of Eqs. (61) and (62) depends on the pressure. For the maximum pressure used in this study (up to 100 GPa) $n=10$ gives sufficiently good result.

If the pressure derivative of the bulk modulus is constant and the temperature has no effect on the volume coefficient of thermal expansion, that is, $b=0$ and $d=0$, then Eqs. (59)–(62) can be simplified as

$$V = nV_0^m e^{-p/(ap+B_0)+(\alpha_0+cp)T} \tag{63}$$

and

$$T = \frac{\ln\left(\dfrac{V}{V_0}\right) + \dfrac{p}{B_0 + ap}}{\alpha_0 + cp} \quad \text{(S-E-5)}. \tag{64}$$

Using Eqs. (61) and (62) and substituting

$$f^n(p) = -(B_0 + ap_{n-1})\left[(\alpha_0 + cp_{n-1})T - \ln\left(\frac{V}{V_0}\right)\right], \tag{65}$$

the pressure can be determined.

Investigating highly symmetrical atomic arrangements linear correlation between the volume coefficient of thermal expansion and the thermal heat capacity was detected.[45] Based on this correlation the integral

$$\int_{T=0}^{T} \alpha_{V_p} dT \tag{66}$$

is approximated by an area of trapezoid (Fig. 3) The integral below the Debye temperature, T_θ, is then

$$\int_{T=0}^{T \leqslant T_\theta} \alpha_{V_p}(T)dT \approx \left(\frac{\alpha_{V_p}T^2}{2T_\theta}\right)_{T \leqslant T_\theta}, \tag{67}$$

while at temperatures higher than the Debye temperature is

$$\int_{T_\theta}^{T} \alpha_{V_p}(T)dT \approx [\alpha_{V_p}(T - T_\theta)]_{T_\theta}^{T > T_\theta}. \tag{68}$$

Combining the two parts Eqs. (67) and (68) gives the general formula

$$\int_{T=0}^{T} \alpha_{V_p}(T)dT \approx H(T)\frac{\alpha_{V_p}T^2}{2T_\theta} + [1 - H(T)]\alpha_{V_p}\left(T - \frac{T_\theta}{2}\right), \tag{69}$$

where $H(T)$ is the Heaviside or unit step function defined as

$$H(T) = \begin{cases} 0 & \text{if } T > T_\theta \\ 1 & \text{if } T \leqslant T_\theta. \end{cases} \tag{70}$$

Substituting Eq. (69) into Eq. (63) gives

$$V = nV_0^m e^{-p/(ap+B_0)+H(T)(cp+\alpha_0)T^2/2T_\theta+[1-H(T)](cp+\alpha_0)(T-T_\theta/2)}. \tag{71}$$

$T_\theta = 1100$ K value was used for the calculations.[46] Assuming a linear pressure dependence for the Debye temperature requires the introduction of an additional multiplier g as follows.

$$T_\theta(p) = gp + T_\theta(p = 0). \tag{72}$$

Equation (71) can be written then as

$$V = nV_0^m e^{-p/(ap+B_0)+H(T)[(cp+\alpha_0)T^2/2(gp+T_\theta)]+[1-H(T)](cp+\alpha_0)[T-(gp+T_\theta)/2]} \quad \text{(Debye + Pressure)}. \tag{73}$$

The validity of Eqs. (59), (63), (71), and (73) will be tested to experiments and I will label these equations as S-E-7, S-E-5, Debye, and Debye+pressure, respectively.

V. TESTING THE EOS TO EXPERIMENTS OF PEROVSKITE

Perovskite, the most abundant mineral of the mantle, has been extensively investigated at high pressures and temperatures. The availability of the wide pressure and temperature range experiments makes this mineral ideal for thermodynamic studies. Experiments up to $25-30$ GPa pressure usually use a multianvil apparatus while at higher pressures diamond anvil cells (DACs) are used. The experimental results of multianvil press[47–51] and diamond anvil[52–54] are used in this study. The experiments cover the pressure $0-109$ GPa, and the temperature $293-2199$ K ranges. The distribution of the 269 experiments is shown in Fig. 4.

A. Fitting criteria

The fitting accuracy of empirical EOSs with the same number of parameters is evaluated by correlation coefficients and root-mean-square deviation (RMSD). The fit quality of models using different numbers of parameters cannot be

evaluated by their correlation coefficients only.[55–57] The test devised assessing the right level of complexity is the Akaike Information Criteria (AIC).[58,59] Assuming normally distributed errors, the criterion is calculated as

$$\text{AIC} = 2k + n \ln\left(\frac{\text{RSS}}{n}\right), \tag{74}$$

where n is the number of observations, RSS is the residual sum of squares, and k is the number of parameters. The preferred model is the one which has the smallest AIC value.

B. Fitting parameters

The fitting parameters, correlation coefficient, RMSD, and AIC were calculated for Eqs. (59), (63), (71), and (73). The best fit is achieved by Eq. (63). The trapezoid approximations used for the volume coefficient of thermal expansion in Eqs. (71) and (73) did not increase the fitting. The explanation could be that the introduced error in the low temperatures is small and overridden by the better fitting at higher temperatures. The parameters providing the best fit are $B_0 = 267.5$ GPa, $V_0 = 24.284$ cm^3, $\alpha_0 = 2.079 \times 10^{-5}$ K^{-1}, $\partial B_0/\partial p = 1.556$, and $\partial \alpha_0/\partial p = -1.098 \times 10^{-7}$ K^{-1} GPa^{-1}. Previous studies (Refs. 1 and 51 and references therein) reported

TABLE II. *p-V* fitting parameters and results. The values in the parentheses are fixed. The numbers following the name of the EOS represent the number of parameters left open for the fitting.

	a	B_{0T} (GPa)	V_{0T} (cm^3)	$B_{0T'}$	$B_{0T'''}$	R	RMSD	AIC
T=300–500 K					**N=86**			
$V(p,T)$ (S-E-5-0)							0.045	−534.2
$V(p,T)$ (S-E-5)						0.999 672 1	0.043	−530.3
$V(p)$ (S-E-5) (T=332 K)						0.999 487 89	0.054	−491.9
$V(p)$ (K_T conv.; 3)	1.441	268.2	24.457			0.999 487 89	0.054	−495.9
$V(p)$ (Roy-Roy; 3)		267.1	(24.473)	−0.537	−0.001 68	0.999 476 92	0.055	−494.1
$p(V,T)$ (S-E-5-0)							0.766	−45.8
$p(V,T)$ (S-E-5)							0.952	1.5
$p(V)$ (S-E-5) (T=332 K)							1.161	35.6
$p(V)$ (Birch; 3)		256.0	24.473	3.832		0.999 343 94	1.059	15.9
$p(V)$ (Vinet; 3)		254.5	24.475	3.976		0.999 341 35	1.061	16.2
$T(V,p)$ (S-E-5-0)							120.8	824.6
$T(V,p)$ (S-E-5)							61.4	726.4
T=300–700 K					**N=38**			
$V(p,T)$ (S-E-5-0)							0.042	−240.5
$V(p,T)$ (S-E-5)						0.999 379 01	0.038	−238.1
$V(p)$ (S-E-5)						0.999 187 84	0.044	−227.9
$V(p)$ (K_T conv.; 3)	1.433	271.7	24.571			0.999 187 84	0.044	−231.9
$V(p)$ (Roy-Roy; 3)		264.4	(24.604)	0.0161	−0.003 75	0.999 115 65	0.046	−228.7
$p(V,T)$ (S-E-5-0)							0.999	−0.1
$p(V,T)$ (S-E-5)							0.534	−37.7
$p(V)$ (S-E-5) (T=610 K)							0.624	−25.8
$p(V)$ (Birch; 3)		256.1	24.604	3.890		0.999 512 69	0.606	−32.1
$p(V)$ (Vinet; 3)		254.8	24.607	4.035		0.999 510 30	0.608	−31.9
$T(V,p)$ (S-E-5-0)							151.4	381.5
$T(V,p)$ (S-E-5)							98.6	358.9
T=700–900 K					**N=42**			
$V(p,T)$ (S-E-5-0)							0.033	−286.2
$V(p,T)$ (S-E-5)						0.999 656 04	0.031	−280.8
$V(p)$ (S-E-5) (T=789 K)						0.999 562 74	0.035	−270.8
$V(p)$ (K_T conv.; 3)	1.448	264.7	24.671			0.999 562 74	0.035	−274.8
$V(p)$ (Roy-Roy; 3)		257.4	(24.707)	−0.740	−0.000 98	0.999 489 30	0.038	−268.2
$p(V,T)$ (S-E-5-0)							0.929	−6.2
$p(V,T)$ (S-E-5)							0.414	−64.1
$p(V)$ (S-E-5) (T=789 K)							0.483	−51.1
$p(V)$ (Birch; 3)		249.2	24.707	3.971		0.999 796 50	0.449	−61.2
$p(V)$ (Vinet; 3)		246.7	24.713	4.171		0.999 794 72	0.451	−60.9
$T(V,p)$ (S-E-5-0)							144.6	417.8
$T(V,p)$ (S-E-5)							100.2	397.0
T=900–1100 K					**N=28**			
$V(p,T)$ (S-E-5-0)							0.041	−178.6
$V(p,T)$ (S-E-5)						0.999 622 91	0.040	−170.7
$V(p)$ (S-E-5) (T=975 K)						0.999 488 23	0.046	−162.1
$V(p)$ (K_T conv.; 3)	1.585	246.2	24.837			0.999 488 23	0.046	−166.1
$V(p)$ (Roy-Roy; 3)		247.4	(24.854)	0.567	−0.0062	0.999 438 99	0.048	−163.5
$p(V,T)$ (S-E-5-0)							0.545	−34.0
$p(V,T)$ (S-E-5)							0.601	−18.5
$p(V)$ (S-E-5) (T=975 K)							0.712	−9.1
$p(V)$ (Birch; 3)		236.0	24.854	4.210		0.999 703 97	0.658	−17.4
$p(V)$ (Vinet; 3)		232.9	24.862	4.453		0.999 711 31	0.650	−18.1
$T(V,p)$ (S-E-5-0)							89.9	251.9
$T(V,p)$ (S-E-5)							136.8	275.6
T=1100–1300 K					**N=26**			
$V(p,T)$ (S-E-5-0)							0.034	−175.6
$V(p,T)$ (S-E-5)						0.999 828 64	0.030	−173.1
$V(p)$ (S-E-5) (T=1179 K)						0.999 663 71	0.041	−155.6

TABLE II.   (*Continued.*)

	a	B_{0T} (GPa)	V_{0T} (cm^3)	$B_{0T'}$	$B_{0T'''}$	R	RMSD	AIC
$V(p)$ (K_T conv.; 3)	1.589	236.9	25.015			0.999 644 80	0.044	−138.1
$V(p)$ (Roy-Roy; 3)		243.9	(25.006)	0.649	−0.0066	0.999 565 43	0.048	−133.5
$p(V,T)$ (S-E-5-0)							0.794	−12.0
$p(V,T)$ (S-E-5)							0.636	−13.3
$p(V)$ (S-E-5) ($T=1179$ K)							0.772	−3.5
$p(V)$ (Birch; 3)		229.3	25.006	4.264		0.999 734 50	0.775	−5.7
$p(V)$ (Vinet; 3)		223.5	25.030	4.589		0.999 740 31	0.766	−6.2
$T(V,p)$ (S-E-5-0)							131.7	253.8
$T(V,p)$ (S-E-5)							137.4	266.0
$T=1300$–1500 K					**$N=17$**			
$V(p,T)$ (S-E-5-0)							0.041	−108.2
$V(p,T)$ (S-E-5)						0.999 729 10	0.038	−101.4
$V(p)$ (S-E-5) ($T=1362$ K)						0.999 691 73	0.040	−99.2
$V(p)$ (K_T conv.; 3)	1.379	267.5	24.899			0.999 716 64	0.040	−84.3
$V(p)$ (Roy-Roy; 3)		250.8	(25.039)	0.641	−0.006 42	0.999 639 13	0.045	−81.0
$p(V,T)$ (S-E-5-0)							0.694	−12.4
$p(V,T)$ (S-E-5)							0.627	−5.9
$p(V)$ (S-E-5) ($T=1362$ K)							0.762	0.8
$p(V)$ (Birch; 3)		235.9	25.039	4.094		0.999 821 65	0.678	−4.9
$p(V)$ (Vinet; 3)		227.5	25.081	4.456		0.999 823 55	0.675	−5.0
$T(V,p)$ (S-E-5-0)							113.9	161.0
$T(V,p)$ (S-E-5)							120.4	172.9
$T=1500$–1700 K					**$N=13$**			
$V(p,T)$ (S-E-5-0)							0.041	−83.2
$V(p)$ (K_T conv.; 3)	2.064	115.1	26.768			0.999 491 13	0.037	−60.1
$V(p)$ (Roy-Roy; 3)		240.3	(25.010)	3.932	−0.0205	0.999 728 32	0.046	−55.6
$p(V,T)$ (S-E-5-0)							0.468	−19.7
$p(V)$ (Birch; 3)		240.6	25.010	(4.0)		0.999 821 14	0.804	−0.4
$p(V)$ (Vinet; 3)		247.2	24.962	(4.0)		0.999 816 47	0.814	−0.1
$T(V,p)$ (S-E-5-0)							77.2	113.0
$T=1700$–1900 K					**$N=13$**			
$V(p,T)$ (S-E-5-0)							0.058	−74.2
$V(p)$ (K_T conv.; 3)	2.341	113.3	26.806			0.995 824 39	0.057	−51.2
$V(p)$ (Roy-Roy; 3)		218.7	(25.538)	0.527	−0.006 80	0.995 543 94	0.059	−50.6
$p(V,T)$ (S-E-5-0)							0.630	−9.0
$p(V)$ (Birch; 3)		210.1	25.538	(4.0)		0.996 338 45	0.837	0.4
$p(V)$ (Vinet; 3)		213.6	25.509	(4.0)		0.996 273 91	0.844	0.6
$T(V,p)$ (S-E-5-0)							117.0	123.8

231–273 GPa for the bulk modulus of pure $MgSiO_3$. The calculated parameters of the EOS and the fitting parameters are given in Table I.

Based on visual inspection the residuals seem to be random (Fig. 5). The RMSDs or uncertainties for the five-parameter EOS are 0.043 cm^3, 0.79 GPa, and 125 K for the volume, pressure, and temperature, respectively. These values are very close to the uncertainties of the experiments[60] indicating that the proposed EOS correctly describes the p-V-T relationship of perovskite.

Starting from 300 K the data set was separated into groups covering 200 K temperature range. Within this temperature range it was assumed that the condition is isothermal. For each temperature range the fitting parameters of the most widely used, finite strain, interatomic potential, and empirical isothermal EOSs Birch-Murnaghan [Eq. (17)], Vinet

[Eq. (24)], and Roy-Roy [Eq. (26)], respectively, were determined. The fitting parameters of the conventional bulk modulus, B_T (conv), were also calculated as follows:

$$V = V_{0T}e^{-p/(ap+B_T)} \text{ (copventional)}. \quad (75)$$

Using the parameters determined from the overall fitting the residuals to the experiments were determined. The RMSD and AIC values were calculated for each of the temperature ranges from the residuals.

The fitting of the S-E-5 was also calculated by using the average temperature of the experiments in each temperature region. The fitting parameters of the S-E-5 (p-V) are slightly weaker than the Birch-Murnaghan and Vinet p-V EOSs. The RMSD values of the S-E-5 (p-V) EOS are better than the RMDS values of the Roy-Roy EOS while the AIC values are better in three and weaker in three temperature ranges.

Using the overall parameters of the S-E-5 (*p-V-T*) EOS the RMSD and AIC values are superior in six temperature ranges while in two temperature ranges the conventional equations are better. If the S-E-5 (*p-V-T*) EOS is fitted specifically to the experiments of the given temperature range then the fitting parameters are superior in all temperature ranges. The results are given in Table II.

VI. CONCLUSIONS

It is suggested that the volume is the sum of the initial volume, the thermal volume at the given pressure, and the elastic volume. Definitions describing the relationships of the temperature and pressure to these fundamental volume parts are defined. Using these definitions a semiempirical seven-parameter (*p-V-T*) EOS is derived. The semiempirical EOS is tested to the available high-pressure and temperature experiments of perovskite. Based on the fitting it is suggested that the temperature derivatives of the bulk modulus and the volume coefficient of thermal expansion are zero and that the pressure derivatives of these parameters are constant. The residuals of the EOS and experiments show random distribution for all of the variables. The uncertainties of the fitting are very close to the uncertainties of the experiments.

The most widely used isothermal EOSs, Birch-Murnaghan, Vinet, and Roy-Roy equations were compared to the semiempirical EOS by separating the experiments into 200 K temperature ranges. Under pure isothermal conditions Birch-Murnaghan and Vinet EOS give a slightly better fit to the experiments than the semiempirical *p-V* EOS. Based on the RMSD and AIC values the S-E-5 (*p-V-T*) EOS is superior in every temperature range to the conventional equations.

The additional advantages of the semiempirical EOS are that the expression is simple and allows calculating any of the required variables.

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