Thermodynamics of deep geophysical media

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Abstract. Analysis of thermodynamic properties of geomaterials at high pressures and temperatures existing in the Earth's interior is presented. The presentation includes a summary on the determination of equations of state based on measured properties of minerals, as well as thermodynamic identities and approximate relations between thermodynamic parameters of the second, third, and in some instances, fourth orders. New expressions were derived for the volume dependences of the coefficient of thermal expansion, the Grüneisen parameter, and the Anderson–Grüneisen parameter. Attention is given to the preparation of the database on mineral properties. Several geophysical estimates, including the lower-mantle properties, were obtained. It was shown that the thermal expansivity decreases 4–5 times along the "hot" mantle adiabat as the pressure increases from 0 to 1.4 Mbar. Under the same conditions, the heat capacity C_P drops about 10–15%. The thermal pressure at $T > \Theta$ is linear in temperature, with an accuracy of 1–3%. The parameter $\partial^2 K_T / \partial P \partial T$ at $P = 0$ for mantle minerals was estimated to be $(1 - 3) \cdot 10^{-4}$ K^{-1}. The acceptable ranges of other lower-mantle parameters are $\delta_V^T = K' - \delta_T \geq 0.2$, $q \leq 0.8$, $\gamma \geq 1.1$, $\delta_T \leq 3 - 3.3$, and $\delta_S \leq 1.9 - 2.2$. Deviations from the Mie–Grüneisen equation of state are discussed in relation to the volume- and temperature-dependent Grüneisen parameter.

1. Introduction

Thermodynamically, the Earth is a heat engine described by a variety of parameters that can be determined from equations of state (EOS) and models of condensed media. A great progress has been achieved in the development of such models [e.g., *Jeanloz*, 1983; *Hemley et al.*, 1985, 1987; *Wall et al.*, 1986; *Catti*, 1986; *Cohen*, 1987a, 1987b; *Dovesi et al.*, 1987; *Wolf and Bukowinski*, 1987, 1988; *Wall and Price*, 1988; *Matsui et al.*, 1987; *Matsui*, 1988, 1989; *Price et al.*, 1989; *Catlow and Price*, 1990; *Isaak et al.*, 1990; *Reynard and Price*, 1990; *Agnon and Bukowinski*, 1990a; *Matsui and Price*, 1991; *D'Arco et al.*, 1991; *Walzer*, 1992; *Silvi et al.*, 1993; *Catti et al.*, 1993; *Boison and Gibbs*, 1993]. Nevertheless, practical studies in geophysics are based,

to a large extent, on the use of semi-empirical EOS's [*Birch*, 1952, 1986; *O. Anderson*, 1966b, 1995; *Pankov and Ullmann*, 1979a, 1979b; *D. Anderson*, 1967, 1987, 1989; *Stacey*, 1981; *Leliva-Kopystynski*, 1991; *Bina and Helffrich*, 1992; *Wall et al.*, 1993]. The properties of geomaterials directly determined from laboratory measurements at high pressures and temperatures are necessary for solving many geophysical problems and provide important constraints on the EOS structure.

Since the fundamental paper of *Birch* [1952], a great deal of information has been accumulated on the properties of geomaterials and their geophysical implication [e.g., *Stacey*, 1977a, 1977b, 1992, 1994; *Jeanloz and Thompson*, 1983; *Brown and Shankland*, 1981; *Zharkov and Kalinin*, 1971; *Zharkov*, 1986; *Jeanloz and Knittle*, 1989; *O. Anderson et al.*, 1992a, 1992b; 1993; *Kuskov and Panferov*, 1991; *D. Anderson*, 1989; *O. Anderson*, 1988, 1995].

This paper is devoted to the review of relationships between the basic thermodynamic characteristics and of their variation with pressure and temperature. First, we deal with eight parameters of the second order. We

emphasize their self-consistent determination and the relations to EOS's and give a summary of approaches used to find the empirically based EOS's. An example of the thermodynamically consistent database for mantle minerals is presented. Then, each of the second-order parameters is treated separately: the identities involving their $P - T$ derivatives (third-order parameters) are established and practically useful approximations are analyzed, including some explicit $P - T$ dependences of the second-order parameters. Some estimates for the fourth-order parameters are also given. The relations between various quantities are represented in the form convenient for practical use of experimental data and for theoretical analysis. Finally, a number of estimates are given for the low-mantle properties. Our analysis serves as an addition to the reviews of *O. Anderson* [1995] and *Stacey* [1994].

2. Basic Thermodynamic Relations

In classical thermodynamics, simple systems experiencing reversable changes of state are described by a variety of parameters including the hydrostatic pressure P, temperature T, volume V (or density ρ), and entropy S. The starting point of thermodynamic analysis is the standard expresions for the total thermodynamic differentials [e.g., *Callen*, 1960; *Morse*, 1969; *Kelly*, 1973]

$$dE = TdS - PdV, \tag{1}$$

$$dF = -SdT - PdV, \quad F = E - TS, \tag{2}$$

$$dG = -SdT + VdP, \quad G = F + PV, \tag{3}$$

$$dH = TdS + VdP, \quad H = E + PV, \tag{4}$$

where E is the internal energy, F is the free energy (Helmholtz potential), G is the free enthalpy (Gibbs potential), and H is the enthalpy.

Eight second-order parameters are largely used in geophysics: the volume coefficient of thermal expansion α, the isobaric C_P and isochoric C_V heat capacities, the isothermal K_T and adiabatic K_S bulk moduli, the thermal pressure coefficient τ, and the adiabatic pressure derivative of temperature (adiabatic temperature gradient in pressure) τ_S. The respective definitions of these parameters are

$$\alpha = V^{-1} \left(\frac{\partial V}{\partial T} \right)_P, \tag{5}$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P,$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V, \tag{6}$$

$$K_T = -V \left(\frac{\partial P}{\partial V} \right)_T, \quad K_S = -V \left(\frac{\partial P}{\partial V} \right)_S, \tag{7}$$

$$\gamma = \frac{\alpha K_T V}{C_V}, \tag{8}$$

$$\tau = \left(\frac{\partial P}{\partial T} \right)_V, \tag{9}$$

$$\tau_S = \left(\frac{\partial T}{\partial P} \right)_S. \tag{10}$$

By equating the cross derivatives of the four thermodynamic potentials, we obtain the Maxwell relations [see, e.g., *Stacey*, 1977a]

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V = -\gamma \frac{T}{C_V}, \tag{11}$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V = \alpha K_T, \tag{12}$$

$$- \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P = \alpha V, \tag{13}$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P = \frac{\gamma T}{K_S} = \frac{\alpha V T}{C_P}. \tag{14}$$

Moreover, it is easily shown that the second derivative of each of these potentials can be expressed in terms of the above parameters or coefficients; i.e., we may write the matrix

$$\begin{pmatrix} \left(\frac{\partial^2 E}{\partial V^2} \right)_S & \frac{\partial^2 E}{\partial V \partial S} & \left(\frac{\partial^2 E}{\partial S^2} \right)_V \\ \left(\frac{\partial^2 H}{\partial P^2} \right)_S & \frac{\partial^2 H}{\partial P \partial S} & \left(\frac{\partial^2 H}{\partial S^2} \right)_V \\ \left(\frac{\partial^2 F}{\partial V^2} \right)_T & \frac{\partial^2 F}{\partial V \partial T} & \left(\frac{\partial^2 F}{\partial T^2} \right)_V \\ \left(\frac{\partial^2 G}{\partial P^2} \right)_T & \frac{\partial^2 G}{\partial P \partial T} & \left(\frac{\partial^2 G}{\partial T^2} \right)_P \end{pmatrix}$$

$$\tag{15}$$

$$= \begin{pmatrix} \frac{K_S}{V} & -\gamma \frac{T}{V} & \frac{T}{C_V} \\ -\frac{V}{K_S} & \tau_S & \frac{T}{C_P} \\ \frac{K_T}{V} & -\tau & -\frac{C_V}{T} \\ -\frac{V}{K_T} & \alpha V & -\frac{C_P}{T} \end{pmatrix}.$$

The number of independent second-order parameters is obviously three, and consequently, the eight second-order parameters introduced above must satisfy five relations. Four of them are (11)–(14), and the fifth can be derived by changing from one pair of characteristic variables to another; specifically,

$$K_S = K_T + \frac{VT}{C_V}\left(\alpha K_T\right)^2,\qquad (16)$$

$$C_P = C_V + VT\alpha^2 K_T.\qquad (17)$$

Thus, if the parameters α, C_P, and K_S (or K_T), as it usually is, are determined experimentally, then the remaining five parameters can be found from the identities

$$\gamma = \frac{\alpha K_S V}{C_P},\ \frac{C_P}{C_V} = \frac{K_S}{K_T} = 1 + \alpha\gamma T,$$

$$\qquad (18)$$

$$\tau = \alpha K_T,\ \tau_S = \frac{\gamma T}{K_S}.$$

We recall two examples of using the thermodynamic relations in geophysics. The first concerns the Williamson–Adams–Birch equation for the density gradient within the Earth [Birch, 1952; D. Anderson, 1989]. We quote this equation in the form

$$\frac{d\rho}{dP} = \frac{1}{\Phi} - \alpha\rho\tau = \frac{1}{\Phi}\left(1 - \gamma\rho C_P t\right),\qquad (19)$$

where ρ and P are the density and pressure in the Earth's interior, respectively, $\Phi = K_S/\rho$ is the seismic parameter, and $\tau = dT/dP - \tau_S$ is the superadiabatic temperature gradient. Equation (19) is easily obtained from

$$d\rho = \left(\frac{\partial\rho}{\partial T}\right)_P dT + \left(\frac{\partial\rho}{\partial P}\right)_T dP$$

with reference to (5), (16) and (14) or (18).

Another example is the adiabatic temperature gradient in depth l within the Earth (see (14)) [e.g., Quareni and Mulargia, 1989]

$$\left(\frac{dT}{dl}\right)_S = \tau_S\rho g = \frac{\gamma Tg}{\Phi},\qquad (20)$$

where g is the gravitational acceleration, and furthermore, the mechanical equalibrium equation $dP/dl = \rho g$ is used.

According to the PREM model [D. Anderson, 1989], $\Phi = 50$, 80, and 117 km^2/s^2 at $l = 400$, 1071, and 2740 km, respectively. Assuming that $\gamma = 1$–1.5 and $T = 1700$, 2200, and 3000 K sequently at the indicated depths [D. Anderson, 1989; Pankov, 1989], (20) yields $(dT/dl)_S = 0.3 - 0.5$ K/km, the value usually cited in geophysical literature.

3. Equations of State and Caloric Functions

The fundamental equation (1) relates five variables two of which are independent. A simple system can therefore be completely described, given knowledge of its thermal $P(V,T)$ and caloric $E(V,T)$ EOS's. The thermal EOS relates the experimental $P - T$ and theoretical $V - T$ variables and is necessary for transforming these variables in analysis of any thermodynamic property [Zharkov and Kalinin, 1971]. The parameters determined by this EOS kind are termed thermal, whereas the quantities derived either from only the caloric EOS or from both thermal and caloric EOS's are thermed caloric. The latter, in particular, include K_S, γ, C_P, and τ_S.

The two EOS kinds are related by the equation

$$\left(\frac{\partial E}{\partial V}\right)_T = -P + \alpha K_T T\qquad (21)$$

whose integral form is

$$E = E(T, V(P,T))$$

$$= \int_0^P \left[\frac{P'V(T,P')}{K_T} - \alpha TV(T,P')\right]dP' + E(T),$$

where the transformation

$$\left(\frac{\partial E}{\partial V}\right)_T = -V^{-1}K_T\left(\frac{\partial E}{\partial P}\right)_T$$

is used, the integration constant is

$$E(T) = E(T, V(T,0)),$$

and the integral is taken along an isotherm. In view of (21), the caloric EOS, $E(V,T)$, is completely determined by the given thermal EOS and function $E(T)$ or $H(T)$ at $P = 0$. It is clear that any of the caloric functions $H(T)$, $S(T)$, $G(T)$, and $C_P(T)$ at $P = 0$ can used for the same purpose, since the following identities take place

$$H(T) = \int_0^T C_P dT + \text{const},\qquad (22)$$

$$S(T) = \int_0^T \frac{C_P}{T}dT + \text{const},\qquad (23)$$

$$G(T) = H(T) - TS(T).$$

The latter formula can be written in another useful form

$$G(T) = G(T^*) - \int_{T^*}^T S(T')dT'$$

$$= G(T^*) - \int_{T^*}^{T} \left(\int_{0}^{T'} \frac{C_P}{T''} dT'' \right) dT' \qquad (24)$$

$$= G(T^*) - (T - T^*)S(T^*) - \int_{T^*}^{T} \left(\int_{T^*}^{T'} \frac{C_P}{T''} dT'' \right) dT',$$

where T^* is a fixed temperature.

For a mineral whose composition can be expressed by a sum of oxides (component), the Gibbs energy is formulated in difference terms

$$G(T) = \Delta H_f(T^*) - T\Delta S_f(T^*)$$

$$- \int_{T^*}^{T} \left(\int_{T^*}^{T'} \frac{\Delta C_P}{T''} dT'' \right) dT' + G_{\text{ox}}(T), \qquad (25)$$

where $\Delta H_f = H - H_{\text{ox}}$, $\Delta S_f = S - S_{\text{ox}}$, and $\Delta C_P = C_P - C_{P\text{ox}}$ are the differences of enthalpy, entropy and heat capacity between the mineral and oxide sum, respectively (with allowance for the stoichiometric coefficients). Expressions of type (25) are often used in calculating phase equilibria [e.g., *Navrotsky and Akaogi,* 1984; *Kuskov and Galimzyanov,* 1986; *Kuskov et al.,* 1989; *Fabrichnaya and Kuskov,* 1991; *Fei and Saxena,* 1986; *Fei et al.,* 1990; *Sobolev and Babeiko,* 1989]. Some authors use an approximation $\Delta C_P = 0$ (or const$\neq 0$; the functions $\Delta C_P(T)$ are sometimes found from empirical formulas of type (67)). In any case, the term $\Delta H_f(T^*)$ in (25) implicitly contains an arbitrary normalizing constant [*Kalinin et al.,* 1991].

Integrating (3) gives

$$G(P, T) = \int_{0}^{P} V(P', T) dP' + G(T), \qquad (26)$$

where $G(T) = G(T, 0)$ is defined by (24) or (25) and can be written in the reduced form

$$G(T) = \Delta H_f(T) - T\Delta S_f(T) + G_{\text{ox}}(T). \qquad (27)$$

Methods for determining EOS's in geophysics can be classified as follows.

(1) The macroscopic approach suggested by *Murnaghan* [1951] and *Birch* [1952] gives the volume dependence of pressure at T (or S) = const in the form [*Ullmann and Pankov,* 1976]

$$P = K_0 f(x; K_0', K_0 K_0'', K_0^2 K_0''', ...), \qquad (28)$$

Hereafter, the values with the subscript 0, unless otherwise specified, are taken at $P = 0$ and an arbitrary temperature, the moduli $K_0 \equiv K_{T0}$, $K_0' = (\partial K_T / \partial P)_{T0},...$

are material parameters, and $x = V/V_0 = \rho_0/\rho$ is the compression ratio parameter. Most data for the material parameter values were obtained at room temperature [e.g., *Sumino and O. Anderson,* 1984]. Among the last experimental achievements are ultrasonic measurements at high pressures [e.g., *Fujisawa,* 1987; *Webb,* 1989; *Yoneda,* 1990; *Liebermann et al.,* 1993], X-ray data of high pressures and high temperatures [e.g., *Yagi et al.,* 1987; *Mao et al.,* 1991; *Fei et al.,* 1992a, 1992b; *Boehler et al.,* 1989], spectoscopic observations of minerals [e.g., *Chopelas,* 1990a, 1990b, 1991a, 1991b, 1993; *Hofmeister,* 1987, 1991a], and high-temperature $P = 0$ measurements of elastic constants by the rectangular parallelepiped technique [*O. Anderson et al.,* 1992a; *O. Anderson,* 1995].

An explicit form of function f in (28) (the volume dependence of pressure) was considered by *Murnaghan* [1951], *Birch* [1952, 1968, 1978, 1986] and others [*Thomsen,* 1970, 1971; *Ahrens and Thomsen,* 1972; *Davies,* 1973; *Ullmann and Pankov,* 1976, 1980; *Pankov and Ullmann,* 1979a; *Stacey,* 1981; *Aidun et al.,* 1984; *Jeanloz,* 1989; *Bina and Helffrich,* 1992; *Isaak et al.,* 1992; *Wall et al.,* 1993]. The most widely used equation of this type is the Birch–Murnaghan EOS.

Elastic moduli and sound velocities in minerals depends first of all on the composition, crystalline structure, pressure, and temperature. Data on these dependences are generalyzed and interpreted in terms of empirical laws such as the Birch's law, the seismic EOS, the law of corresponding states, and a universal EOS [*Birch,* 1961; *O. Anderson and Nafe,* 1965; *D. Anderson,* 1967, 1987; *Chung,* 1973; *Davies,* 1976; *O. Anderson,* 1973; *D. Anderson and O. Anderson,* 1970; *Mao,* 1974; *Kalinin,* 1972; *Schankland and Chung,* 1974; *Campbell and Heinz,* 1992]. These laws enable us to estimate the parameters K_0 and, to a lesser accuracy, K_0' for unmeasured minerals [*D. Anderson,* 1988; *Duffy and D. Anderson,* 1989].

(2) Statistical physics describing the vibrations of atoms in crystals provides the background for microscopic EOS theory including the Mie–Grüneisen EOS [*Grüneisen,* 1926; *Born and Huang,* 1954; *Leibfried and Ludwig,* 1961; *Knopoff,* 1963; *Knopoff and Shapiro,* 1969; *Zharkov and Kalinin,* 1971; *Wallace,* 1972; *Mulargia,* 1977; *Mulargia and Boschi,* 1980; *Hardy,* 1980; *O. Andrrson,* 1980; *Gillet et al.,* 1989, 1990, 1991; *Richet et al.,* 1992; *Reynard et al.,* 1992]. This approach also uses the lattice or vibrational Grüneisen parameters, as well as either semiempirical potentials of atomic interactions or the reference (isothermal or adiabatic) $P - V$ relations derived from continuum mechanics [e.g., *Al'tshuler,* 1965; *Zharkov and Kalinin,* 1971; *Ahrens and Thomsen,* 1972; *McQueen,* 1991]. The material parameters in these cases are determined using static and dynamic compression data, elastic constant

measurements, caloric functions, and vibrational spectrums.

(3) Integrating (12) yields the pressure as a sum of two terms: a reference isotherm and the thermal pressure increment ΔP_{th}. This thermodynamic approach based on experimental data has been developed by O. Anderson [1979a, 1979b, 1979c, 1980, 1982, 1984, 1988, 1995] and was used to describe the X-ray and resonance data for a set of minerals [O. Anderson et al., 1982, 1992a; O. Anderson and Yamamoto, 1987; O. Anderson and Zou, 1989; Mao et al., 1991; Fei et al., 1992a, 1992b].

(4) More intricate theoretical EOS models are derived from ab initio calculation using the Hartree–Fock and Thomas–Fermi–Dirak methods, as well as pseudopotential theory, many-term contributions in semiempirical potentials, and molecular dynamics [Hemley et al., 1985, 1987; Isaak et al., 1990; Wolf and Bukowincki, 1987, 1988; Wall and Price, 1988; Wall et al., 1986; D'Arco et al., 1991; Price et al., 1989; Matsui et al., 1987; Matsui, 1988, 1989; Reynard and Price, 1990; Agnon and Bukowinski, 1990a; Walzer, 1992; Cohen, 1987a; Dovesi et al., 1987; Catlow and Price, 1990; Boisen and Gibbs, 1993; Silvi et al., 1993; Catti et al., 1993; Barton and Stacey, 1985].

As mentioned above, the complete description of a simple system requires knowledge of either any of its thermodynamic potentials or its thermal EOS and one of the caloric functions (at $P = 0$). Table 1 lists various approaches to the determination of EOS's, showing which functions must be found from theory or experiment so as to provide such a complete description. These approaches can also be formulated in the form of partial differential equations with appropriately chosen boundary conditions.

4. Thermodynamic Parameters of the Third and Higher Orders

The order of a thermodynamic parameter (characteristic of a matter) is defined by the maximum order of the thermodynamic potential derivative involved to define the thermodynamic parameter. To find all of the third-order parameters (P, V, T, or S derivatives of the second-order parameters), whose total number for the potentials in (1)–(4) is 16, it is sufficient to know four independent and appropriately chosen third-order parameters, in addition to knowledge of the lower-order parameters. Specifically, experiments often provide information on the derivatives $(\partial K_S/\partial P)_T$ (or

$$\left(\frac{\partial K_T}{\partial P}\right)_T \equiv K'), \left(\frac{\partial K_S}{\partial T}\right)_P, \left(\frac{\partial C_P}{\partial T}\right)_P \text{ and } \left(\frac{\partial \alpha}{\partial T}\right)_P.$$

The relationships of these derivatives to other parameters are further discussed in later sections.

To extrapolate data on thermodynamic properties to high pressures and temperatures, the power volume dependence is often applied stating that the logarithmic volume derivative of the parameter considered is a constant [Zharkov, 1986; D. Anderson, 1988, 1989]. The temperature derivative of any parameter A at $P = $ const is represented in the dimensionless form

$$\frac{1}{\alpha}\left(\frac{\partial \ln A}{\partial T}\right)_P = \left(\frac{\partial \ln A}{\partial \ln V}\right)_P$$
$$= \frac{1}{\alpha}\left(\frac{\partial \ln A}{\partial T}\right)_V + \left(\frac{\partial \ln A}{\partial \ln V}\right)_T, \qquad (29)$$

where the first term characterizes the so-called intrinsic anharmonicity and the second is a parameter of the extrinsic anharmonicity related to thermal expansion [Jones, 1976; Smith and Cain, 1980]. Parameter A can be any physical property, such as the transport coefficients or mode Grüneisen parameters [Reynard et al., 1992; Gillet et al., 1989].

5. Thermodynamic Database

The database on properties of minerals, required for geophysical analysis and EOS construction, must include first of all their density and the second and third order thermodynamic parameters. An example of such database for three mantle minerals is given in Tables 2 and 3, and the database for 25 mantle minerals, including their high-pressure phases (and some fictive phases), is presented in Internet [Pankov et al., 1997]. The parameter values in these tables refer to the conditions $P = 0$, $T = 300$ K or $P = 0$ and the temperature indicated. Apart from the second-order thermodynamic parameters, Table 2 includes the molar mass M, mean atomic weight μ, density ρ, the melting temperature T_m, the Debye temperatures Θ (Θ_a is the acoustic temperature, Θ_α is from fitting the Mie–Grüneisen EOS to data on α [Suzuki, 1975a, 1975b], and Θ_{th} is our estimate from data on specific heat), the classical value $C_V = 3R/\mu$ (R is the gas constant), the enthalpy ΔH_f and entropy ΔS_f of mineral formation from oxides, and the estimated thermal pressure $P_{th} \approx 0.5\alpha K_T$. It is important to have mutually consistent values of the second (and higher) order parameters: here, the calculations are based on the input values of K_S (or K_T), α, and C_P. At high temperatures, $T > 300$ K, the α and C_P values were found by the empirical formulas from Fei and Saxena [1987] and Fei et al. [1990, 1991], and for K_S, we give either experimental values or our estimates through the Anderson–Grüneisen parameter δ_S (at 300 K), which is assumed to be a constant (see Table 3 and sections 9 and 10). The values listed in Table 3 are based on the input values of the derivatives $(\partial K_S/\partial P)_T$, $(\partial K_S/\partial T)_P$ (or δ_S),

Table 1. Examples of complete thermodynamic description of a system

Version	Given functions
1	$P(V,T)$ and the temperature dependence of any of the caloric functions $G, H, S, C_P, K_S, \tau_S, \gamma, C_V$ at $P = 0$
2	$F(V,T)$ from statistical physics, resulting in a quasiharmonic or anharmonic EOS with $\gamma(V,T)$ or the Mie-Grüneisen EOS with $\gamma(V)$
3	$P(V, T_0)$ and $E(V,T)$ for $T_0 > 0$
4	$P(V, T_0), C_V(V, T)$ and $E(V)$ for $T = 0, T_0 > 0$
5 *	$P(V, T_0), \tau(V, T)$ and the temperature dependence of any of the caloric functions mentioned in version 1 at $P = 0$
6	$P(V/V_0, K_0, K_0', ...), V_0(T), K_0(T), K_0'(T), ...$ and the temperature dependence of any of the caloric functions mentioned in version 1
7	$P(V, T_0), \tau_S(P, T)$, and any of the functions $C_P(T), \alpha(T), H(T), S(T)$, and $G(T)$ at $P = 0$
8	$P - V$ Hugoniot, $\gamma(V)$, and the Mie-Grüneisen EOS form
9	$K_S(P, T), \alpha(T)$, and $C_P(T)$ at $P = 0$

* The thermal EOS can also be found given the pairs of functions
$P(V, T_0)$ and $\alpha(P, T)$, $P(V, T_0)$ and $K_T(V, T)$, or $V(0, T)$ and $K_T(P, T)$.

$(\partial C_P/\partial T)_P$, and $\hat{\alpha} = \alpha^{-2}(\partial \alpha/\partial T)_P$, as well as on the second-order parameter values given in Table 2. The high-temperature values of the third-order parameters were evaluated using the condition $(\partial K_S/\partial P)_T \approx$ const. Finally, in Table 2 are given the references to sources of thermodynamic data for each of the minerals.

6. The Volume Coefficient of Thermal Expansion

6.1. P–T derivatives

It follows from the identity $\partial^2 V/\partial T \partial P = \partial^2 V/\partial P \partial T$ that [Birch, 1952]

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = \frac{1}{K_T^2} \left(\frac{\partial K_T}{\partial T}\right)_P. \tag{30}$$

This fundamental relation is written in the dimensionless form

$$\delta_T \equiv -\frac{1}{\alpha K_T} \left(\frac{\partial K_T}{\partial T}\right)_P$$

$$= \left(\frac{\partial \ln \alpha}{\partial \ln V}\right)_T = \left(\frac{\partial \ln K_T}{\partial \ln \rho}\right)_P, \tag{31}$$

where the isothermal Anderson–Grüneisen parameter δ_T is introduced [O. Anderson, 1966a, 1967; Barron, 1979].

The variation of α with temperature at $P = $ const is characterized by the parameter $\hat{\alpha}$ [Fürth, 1944; O. Anderson, 1966b; Birch, 1986; O. Anderson et al., 1993]

$$\hat{\alpha} \equiv \frac{1}{\alpha^2} \left(\frac{\partial \alpha}{\partial T}\right)_P$$

$$= \frac{1}{\alpha^2} \left(\frac{\partial \alpha}{\partial T}\right)_V + \delta_T = \left(\frac{\partial \ln \alpha}{\partial \ln V}\right)_P. \tag{32}$$

The term

$$\frac{1}{\alpha^2} \left(\frac{\partial \alpha}{\partial T}\right)_V$$

can be related to the derivatives of C_V and K_T, by making use of the identity $\partial^2 S/\partial V \partial T = \partial^2 S/\partial T \partial V$, which leads to

$$\frac{1}{\alpha^2} \left(\frac{\partial \alpha}{\partial T}\right)_V$$

$$= -\frac{1}{\alpha^2 VT} \left(\frac{\partial C_V}{\partial P}\right)_T - \frac{1}{\alpha K_T} \left(\frac{\partial K_T}{\partial T}\right)_V \tag{33}$$

$$= -\frac{1}{\alpha^2 VT} \left(\frac{\partial C_V}{\partial P}\right)_T + (\delta_T - K').$$

Table 2. Thermodynamic parameters of minerals at normal pressure and twovalues of temperature

Parameter	MgO, periclase 300 K	MgO, periclase 1800 K	Al$_2$O$_3$, corundum 300 K	Al$_2$O$_3$, corundum 1800 K	Mg$_2$SiO$_4$, forsterite 300 K	Mg$_2$SiO$_4$, forsterite 1700 K
M, g/mole	40.32		101.96		140.69	
μ, g/mole	20.16		20.39		20.10	
ρ, g/cm^3	3.585 [1]	3.354 [1]	3.982 [1]	3.831 [1]	3.222 [1]	3.055 [1]
T$_m$, K	3125 [2]		2345 [2]		2163 [2]	
Q$_a$, K	945 [1]	811 [1]	1034 [1]	922 [1]	763 [1]	668 [1]
Q$_{th}$, K*	761	706	966	871	887	763
Q$_\alpha$, K	942 [45]		1031 [45]		732 [45]	
S, J/K mole	26.94 [2]	113.14 [2]	50.92 [2]	256.68 [2]	94.110 [53]	372.48
H, kJ/mole**	5.166 [2]	80.28 [2]	10.016 [2]	192.45 [2]	−43.392***	194.89
ΔS$_f$, J/K mole	0	0	0	0	−1.23	−
ΔH$_f$, kJ/mole	0	0	0	0	−60.64	−
K$_S$, GPa	163.9 [1]	132.7 [1]	253.7 [15]	221.8 [15]	128.7 [1]	103.8 [1]
α, 10^{-5} K^{-1}	3.12 [1]	5.13 [1]	1.62 [1]	3.25 [1]	2.72 [1]	4.62 [1]
C$_P$, J/g K	0.928 [1]	1.358 [1]	0.771 [1]	1.318 [1]	0.840 [1]	1.370 [1]
K$_T$, GPa	161.6	116.6	252.2	204.7	127.4	95.3
γ	1.54	1.50	1.34	1.43	1.29	1.14
C$_V$, J/g K	0.915	1.193	0.766	1.216	0.831	1.258
C$_V^{class}$, J/g K	1.237		1.223		1.241	
$\alpha\gamma$T	0.014	0.138	0.006	0.084	0.011	0.089
$\tau = \alpha$K$_T$, MPa/K	5.04	6.00	4.08	6.65	3.46	4.40
τ_S, K/GPa	2.82	20.0	1.58	11.6	3.00	18.7
P$_{th}$, ГПа	0.717 [1]	9.95 [1]	0.6	4.13 [1]	0.429 [46]	6.30 [1]
Reference	3–12, 32, 35, 46, 49, 53, 68–71, 73–78, 83, 97, 124, 131, 193, 202, 211		12–15, 74, 79–83, 118, 211		2, 11, 12, 22, 32, 45, 66, 69, 74, 83, 89, 95, 97, 113, 126, 128, 129, 178, 190, 191, 194, 201, 204, 206–211	

1. *O. Anderson et al.* [1992a]
2. *Robie et al.* [1978]
3. *Isaak et al.* [1989a]
4. *Isaak et al.* [1990]
5. *Jackson and Niesler* [1982]
6. *O. Anderson and Zou* [1989]
7. *O. Anderson et al.* [1993]
8. *Chopelas* [1990b]
9. *Hemley et al.* [1985]
10. *Sumino et al.* [1983]
11. *O. Anderson and Suzuki* [1983]
12. *Sumino and O. Anderson* [1984]
13. *White and Roberts* [1983]
14. *Furukawa et al.* [1968]
15. *Goto et al.* [1989]
22. *Jeanloz and Thomsen* [1983]
32. *Richet et al.* [1989]
35. *M. Liu and L. Liu* [1987]
45. *Duffy and D. Anderson* [1989]
49. *Fei et al.* [1991]
53. *Fei et al.* [1990]

66. *Kuskov and Galimzyanov* [1986]
68. *Duffy and Ahrens* [1993]
69. *Fei and Saxena* [1986]
70. *Carter et al.* [1971]
71. *Vassiliou and Ahrens* [1981]
73. *Boehler* [1982]
74. *Berman* [1988]
75. *Spetzler* [1970]
76. *Mao and Bell* [1979]
77. *Yoneda* [1990]
78. *Chopelas and Nicol* [1982]
79. *Richet et al.* [1988]
80. *Mao et al.* [1986]
81. *Gupta* [1983]
82. *Finger and Hazen* [1978]
83. *Ullmann and Pankov* [1976]
89. *Chopelas* [1990a]
95. *O. Anderson and Goto* [1989]
97. *Suzuki* [1975a]
113. *Hofmeister* [1987]
118. *McMillan and Ross* [1987]

124. *Matsui* [1989]
126. *Gillet et al.* [1991]
128. *Hofmeister et al.* [1989]
129. *Chopelas* [1991b]
131. *Wolf and Bukowinski* [1988]
178. *Graham et al.* [1982]
188. *Weidner and Hamaya* [1983]
190. *Yeganeh-Haeri and Vaugham,* [1984]
191. *Webb* [1989]
193. *O. Anderson et al.* [1992b]
194. *Reynard et al.* [1992]
201. *Saxena* [1988]
202. *Saxena and Zhang* [1990]
204. *Hazen and Finger* [1989]
206. *Fiquet et al.* [1992]
207. *Will et al.* [1986]
208. *Iishi* [1978]
209. *Hazen* [1976]
210. *Webb and Jackson* [1985]
211. *Richet and Fiquet* [1991]

* Θ_{th} from the Debye C$_V$ at T = 300 K and from the classical approximation $S = \dfrac{RM}{\mu}(4 - 3\ln\Theta/T)$ for $T > \Theta$.

** It is assumed that $H = 0$ at $T = 0K$ for quartz, periclase, and coesite; for other minerals, $H(T)$ is normalized relative to the sum oxides at T = 300 K.

*** $H = \Delta H_f + \sum \nu_i H_i$.

Table 3. Third-order thermodynamic parameters of minerals at normal pressure and two values of temperature*

Parameter	MgO, periclase		Al_2O_3, corundum		Mg_2SiO_4, forsterite	
	300 K	1800 K	300 K	1800 K	300 K	1700 K
$(\partial K_S/\partial P)_T$	4.13 [5]***	4.13	4.28 [12]	4.28	5.1 [36]**	5.1
$(\partial K_T/\partial P)_T \equiv K'$	4.16	4.42	4.30	4.37	5.12	5.23
$(\partial K_S/\partial P)_S$	4.09	3.70	4.26	4.05	5.05	4.75
δ_S	2.83 [1]	3.12 [1]	3.83 [1]	2.68 [1]	4.45	3.96 [1]
δ_T	4.96	4.83	5.99	4.42	5.89	5.27
δ_V^T	−0.80	−0.42	−1.69	−0.05	−0.77	−0.04
δ_V^S	1.24	0.51	0.42	1.27	0.59	0.72
$\hat{\alpha}$	46 [1]	3.5 [1]	140 [1]	4.9 [1]	42 [1]	5.9 [1]
$(\partial \ln C_P/\partial \ln T)_P$	0.43 [1]	0.15 [1]	0.67 [1]	0.16 [1]	0.53 [1]	0.23 [1]
$(\partial \ln C_P/\partial \ln T)_V$	0.42	0.10	0.67	0.13	0.53	0.20
$(\partial \ln C_P/\partial \ln V)_T$	0.65	0.55	0.84	0.46	0.47	0.44
$(\partial \ln C_V/\partial \ln T)_P$	0.41	−0.01	0.66	0.06	0.52	0.13
$(\partial \ln C_V/\partial \ln T)_V$	0.41	0.01	0.66	0.06	0.51	0.14
$(\partial \ln C_V/\partial \ln V)_T$	0.56	−0.24	0.79	0.04	0.39	−0.08
$\dfrac{C_P}{\alpha^2}\left(\dfrac{\partial \alpha/C_P}{\partial T}\right)_P$	0.06	1.88	2.14	2.16	−23.0	1.47
$(\partial \ln \gamma/\partial \ln V)_T \equiv q$	1.24	1.66	1.90	1.01	1.38	1.12
$\alpha^{-1}(\partial \ln \gamma/\partial T)_V$	−2.96	−1.90	−2.5	−0.52	−30.0	−2.60
$(\partial \ln \tau_S/\partial \ln V)_T \equiv n$	5.31	5.29	6.15	4.96	6.43	4.74
$\alpha^{-1}(\partial \ln \tau_S/\partial T)_P$	108	137	209	20.3	99.6	15.2

* Under the assumption of $(\partial K_S/\partial P)_T$ = constant. Placed in brackets are the references (see Table 2).

** 4.9–5.3 [12]

*** 3.85–4.49 [12]

Similarly, the identity $\dfrac{\partial^2 S}{\partial P \partial T} = \dfrac{\partial^2 S}{\partial T \partial P}$ yields

$$\hat{\alpha} = -1 - \frac{1}{\alpha^2 VT}\left(\frac{\partial C_P}{\partial P}\right)_T$$

$$= -1 + \frac{1 + \alpha\gamma T}{\alpha\gamma T}\left(\frac{\partial \ln C_P}{\partial \ln V}\right)_T, \qquad (34)$$

where the convenient dimensionless product is used

$$\alpha\gamma T = \frac{K_S}{K_T} - 1 = \frac{C_P}{C_V} - 1.$$

Birch [1952] pointed out that parameter δ_T for various materials usually lies between 4 and 8 (at normal conditions), which was borne out by subsequent studies [see, e.g., *Sumino and O. Anderson*, 1984; *O. Anderson et al.*, 1992a] some exclusions are also encountered: e.g., $\delta_T \approx 1$ for KMnF$_3$ and $\delta_T \approx 77$ for Re$_2$O$_3$.

The parameter $\hat{\alpha}$ values at normal conditions are commonly greater than the δ_T values [*Birch*, 1952; *O. Anderson et al.*, 1992a]. The data and estimates listed in

the tables of *Pankov et al.* [1997] for 25 minerals fall into the range $10 \lesssim \hat{\alpha} \lesssim 270$. However, at high temperatures $(T > \Theta)$, the δ_T and $\hat{\alpha}$ values become closer to each other, and their concidence would mean that α were dependent only on volume (i.e., the intrinsic anharmonicity were suppressed).

The following three assumptions and their consequences are of interest:

(1) The specific heat C_V is independent of pressure, i.e., $C_V = C_V(T)$, as in the Van der Vaals or Hildebrand EOS's [*O. Anderson*, 1979a], or alternatively, C_V = const, as in the classical limit at $T > \Theta$. Then, from (32) and (33),

$$\frac{1}{\alpha^2}\left(\frac{\partial \alpha}{\partial T}\right)_V = \delta_T - K', \qquad \hat{\alpha} = 2\delta_T - K' \qquad (35)$$

At $P = 0$, $\delta_T \geq K'$ is the common case.

(2) K_T depends only on volume; the $K_T(V)$ approximation is often warranted at $T > \Theta$ [*O. Anderson*, 1982; *D. Anderson*, 1988, 1989]. Then, $(\partial K_T/\partial T)_V = 0$, and from (29) and (31), we have $K' = \delta_T$; i.e., δ_T either

depends only on volume or is a constant (leading to the Murnaghan EOS (44)).

(3) If both conditions (1) and (2) take place, then $\alpha = \alpha(V)$ and $K' = \delta_T = \hat{\alpha}$ (that is either volume-dependent or a constant).

6.2. Explicit volume (pressure) dependences of α at $T = \mathrm{const}$

In most of the interiror of the Earth, $T > \Theta$ and α minimally depends on temperature. Consider a few approximate relations for evaluating the isothermal or adiabatic variation of α.

6.2.1. By using the general EOS form of (28) and the formula (12), we find the expansion for α

$$\frac{\alpha}{\alpha_0} = 1 - \delta_{T0} \frac{P}{K_T} + \frac{K_0}{\alpha_0 K_T} \times$$

$$\times \left[\frac{\partial f}{\partial K'_0} \frac{dK'_0}{dT} + \frac{\partial f}{\partial (K_0 K''_0)} \frac{d(K_0 K''_0)}{dT} + \cdots \right]. \quad (36)$$

If only two first terms are retained in (36), then the formula of *Birch* [1952, 1968] derives. It should be noted that α in this formula changes its sign at $K_T/P = \delta_{T0}$ (the condition that may be achieved in the lower mantle at $K_T/P = 4.7$). Moreover, in this case, δ_T given by most of the type (28) EOS's increases with pressure instead of its usual decrease (see section 9). It was shown, however, that such a change in the α sign is forbidden thermodynamically [*Pankov, 1992*].

As an example of using (36), we calculated $\alpha(P/K_0)$ with the help of the EOS form proposed by *Ullmann and Pankov* [1976, 1980], for which

$$f(x, K'_0) = -yy', \quad y = \frac{1}{u}(x^u - 1),$$

$$u = \frac{1}{3}(2 - K'_0), \quad y' = \frac{dy}{dx}, \quad (37)$$

so that

$$K_T = K_0 x \left(y^2 + yy'' \right). \quad (38)$$

First, we set $dK'_0/\partial T = 0$ and neglect terms containing K''_0, K'''_0, ... The α/α_0 versus P/K_0 curves, obtained for resonable values $K'_0 = 3$ and 4 and $\delta_{T0} = 2, 4$, and 6, are shown in Figure 1. For change from P to volume, Figure 2 gives the variation of P/K_0 with x. We see, in particular, that the δ_{T0} values significantly affect the estimated α under lower-mantle conditions (at the base of the mantle compressed along its "hot" adiabat, $x \approx 0.7$ and $P/K_0 \approx 0.70$ for $K_0 \approx 1.9 - 2.0$ Mbar and $K'_0 = 3.8 - 4.1$ [*D. Anderson*, 1989]). Furthermore, the approximation used for α may lead to the nonrealistic result $\alpha < 0$ within the lower mantle.

To illustrate the influence of the non-zero $dK'_0/\partial T$ values, now we allow for the third term in (36), with the setting $dK'_0/\partial T = \pm 2 \cdot 10^{-3}$ K^{-1} (the values that we estimated for NaCl from data discussed by Birch [*Birch, 1978*]). The value $2 \cdot 10^{-3}$ K^{-1} is not realistic since it results in the increase of α with pressure (Figures 1 and 3). On the other hand, the negative value $-2 \cdot 10^{-3}$ K^{-1} is too small, since it considerably lessens the pressure at which the condition $\alpha \leq 0$ mentioned above is reached.

The approximations $K' = \delta_T$ (see above) and $\delta_T \approx$ constant at $T > \Theta$ imply a very weak temperature dependence of K'. The lattice dynamics models show that K' for MgSiO$_3$ perovskite varies less than 10% in the temperature range of 300–2000 K ($dK'_0/\partial T \leq 2 \cdot 10^{-4}$ K^{-1}). The theoretical PIB model for MgO [*Isaak et al., 1990; O. Anderson et al., 1993*] shows that $dK'_0/\partial T$ somewhat increases with temperature in the same interval of 300–2000 K, with the values ranging, on average, from $2.8 \cdot 10^{-4}$ to $4.2 \cdot 10^{-4}$ K^{-1}. Values of a similar order follow from the approximation $d \ln K'_0/d \ln \rho = -1$ indicated by *D. Anderson* [1989] for PREM.

The derivative dK'_0/dT can also be estimated by the approximation $K_T = K_T(V)$ (i.e., $K' = \delta_T$ and (70) are allowed for) noted above

$$\frac{\partial}{\partial T} \left(\frac{\partial K_T}{\partial P} \right)_T = \left(\frac{\partial K'}{\partial T} \right)_P$$

$$= \frac{\partial}{\partial P} \left(\frac{\partial K_T}{\partial T} \right)_P = -\alpha K_T K'' \quad (39)$$

where the primes indicate pressure derivatives. With $\alpha \approx 3 \cdot 10^{-5}$ K^{-1} and $-K_T K'' \approx 5-10$ [e.g., *Pankov and Ullmann, 1979a; Hofmeister, 1991b*], we find $dK'_0/\partial T \approx (1-3) \cdot 10^{-4}$ K^{-1}, which is close to the estimates found above.

Finally, we can use identity (91) from section 9, which of course leads to (39) for $K' = \delta_T$ (see (71)). Although the terms in (91) are close to each other, the reasons given below justify the inequality $(\partial \delta_T/\partial P)_T \lesssim 0$, and consequently,

$$\left(\frac{\partial K'}{\partial T} \right)_P \gtrsim \alpha \delta_T (\delta_T - K'). \quad (40)$$

Substituting the parameter values from Tables 2 and 3 (see also tables in *Pankov et al.* [1997]) into the right side of the above, we find

$$\frac{dK'_0}{dT} \gtrsim (1 - 5) \cdot 10^{-4} \mathrm{K}^{-1}.$$

It should be emphasized that the correction to α in (36) related to this derivative enables us to avoid negative or increased values of α at high pressures. The effect of the value $dK'_0/dT = 2 \cdot 10^{-4}$ K^{-1} on the α curve for $K'_0 = \delta_{T0} = 4$ is shown in Figure 1.
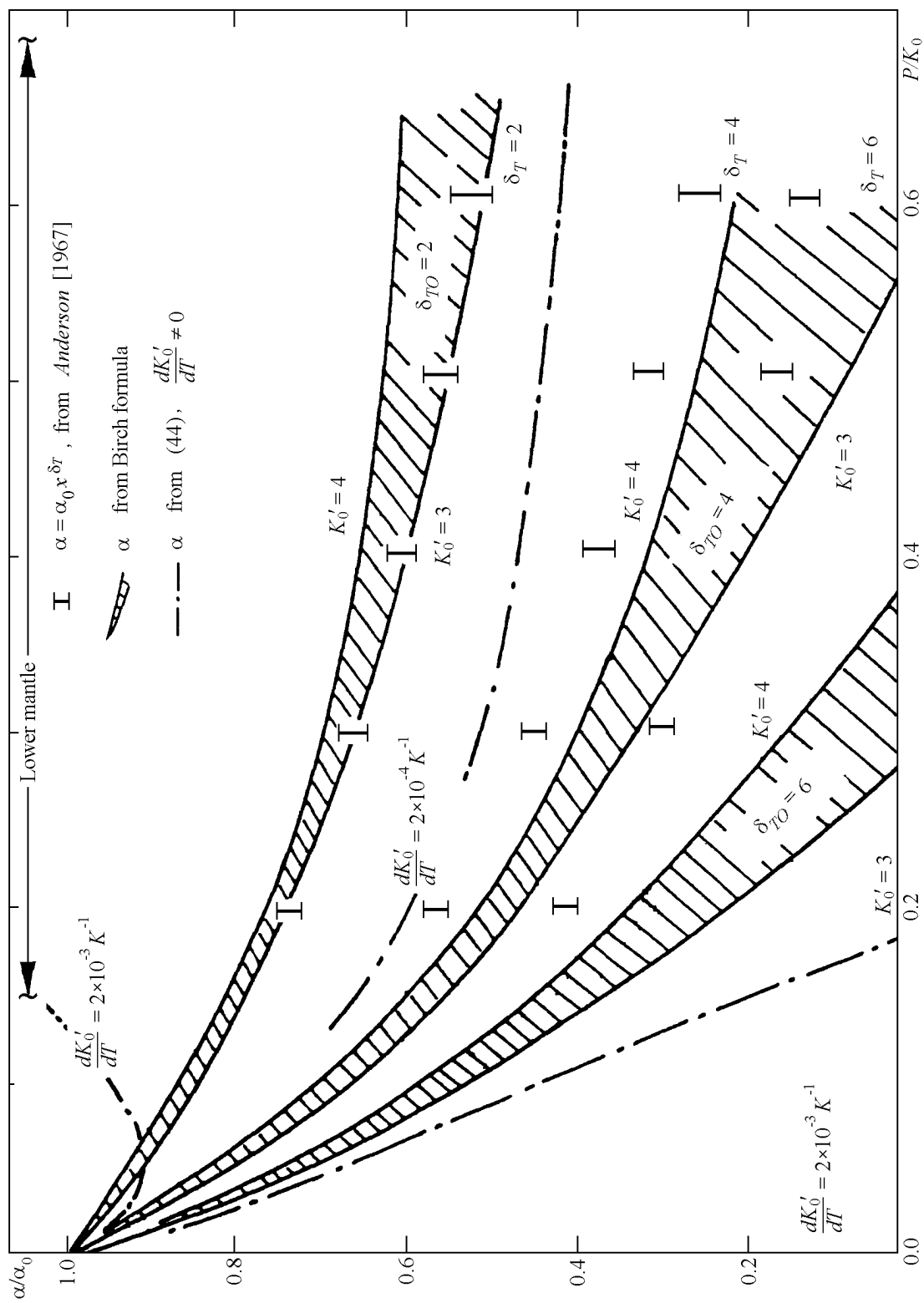
Figure 1. α/α_0 versus P/K_0. (1) The vertical bars show the dependence $\alpha = \alpha_0 x^{\delta_T}$, where $\delta_T = 2, 4$, and 6; the upper and lower ends of the bars are for $K_0' = 3$ and 4, respectively. (2) The hatched bands are α by the Birch formula (36), where only two first terms are taken into account, i.e., $dK_0'/dT = 0$; $\delta_{T0} = 2, 4$, and 6, respectively, and the upper and lower ends of the bands are for $K_0' = 4$ and 3, respectively. (3) The dot-and-dash lines are α by the generalized Birch formula (36) with allowance for the parameter $dK_0'/\alpha T$, whose values are indicated on the plot ($\alpha_0 = 3 \cdot 10^{-5}$ K^{-1} is assumed). The pressure and volume in all these cases are related by equation (37) (see Figure 2).
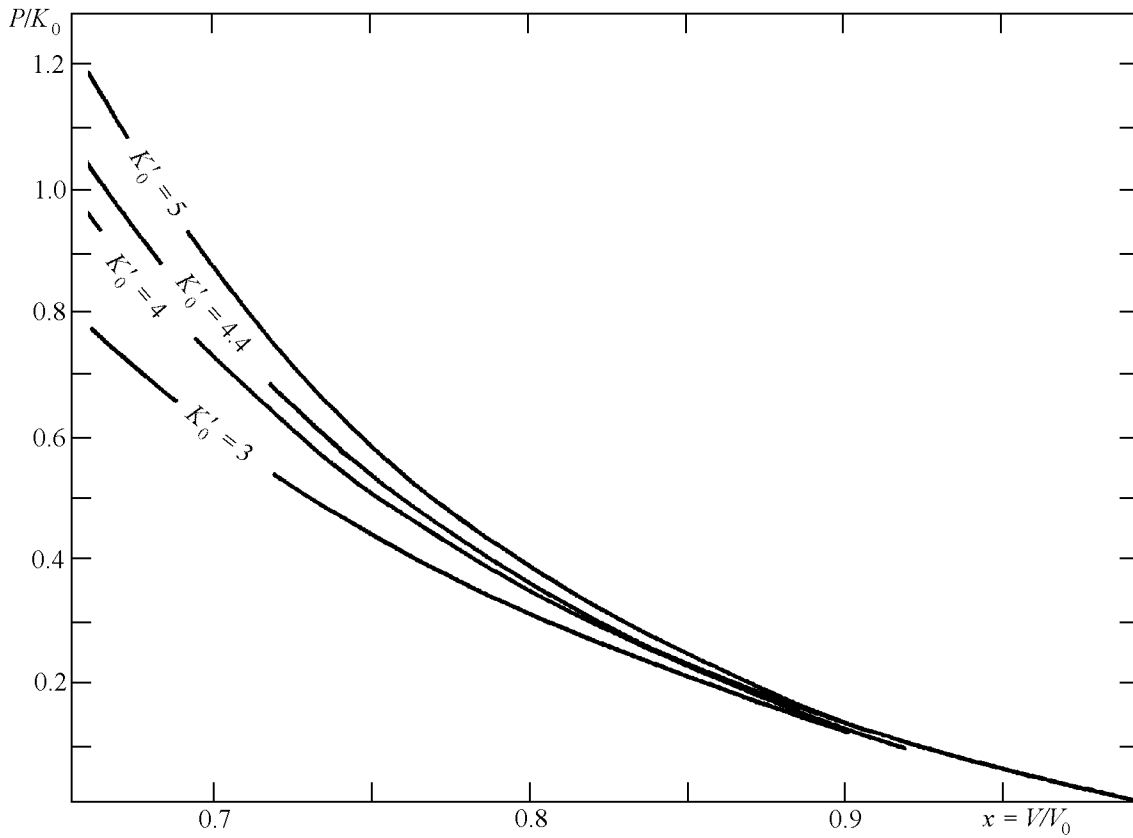
Figure 2. Relative pressure versus relative volume by equation (37) [*Ullmann and Pankov*, 1976, 1980]

6.2.2. *O. Anderson* [1967] derived the power law

$$\alpha = \alpha_0 x^{\delta_{T0}}, \tag{41}$$

by integrating (30) and (8), provided that

$$\left(\frac{\partial C_V}{\partial P}\right)_T \approx \left(\frac{\partial C_V}{\partial P}\right)_S \approx 0,$$

which yields

$$\delta_T = K' - 1 + q, \tag{42}$$

where parameter q is defined as

$$q \equiv \left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_T. \tag{43}$$

Moreover, he assumed that $\delta_T \approx K' \approx$ const. The constancy of K' (or alternatively, $K' = K'(T)$) leads to the Murnaghan EOS (of a type of (28))

$$P = \frac{K_0}{K_0'} \left(x^{-K_0'} - 1\right), \qquad K_T = K_0 x^{-K_0'}. \tag{44}$$

It is clear that (41) simply follows from the definition of δ_T by (31) on the condition that δ_T is either only temperature-dependent, $\delta_T = \delta_T(T)$, or is a constant; moreover, (44) can be replaced with any suitable approximation to the isotherm $P(V, T_0)$.

The two functions $\alpha(V, T)$ and $P(V, T)$, however, cannot be picked independently. For example, the EOS can apparently be defined by specifying $\alpha(V, T)$ and $P(V, T_0)$. At this point, it is appropriate to discuss the following generalization of the results mentioned in various papers [*Birch*, 1968; *Clark*, 1969; *O. Anderson*, 1986; *D. Anderson*, 1989]. Consider four statements: (*1*) the Murnaghan EOS (44) is valid, where it is assumed that K_0 is a function of temperature, $K_0(T)$, and K_0' is either a constant or depends only on temperature; (*2*) $(\partial \delta_T / \partial P)_T = 0$ (i.e., $\delta_T =$ const or $\delta_T = \delta_T(T)$); (*3*) $(\partial K' / \partial T)_P = 0$; (*4*) $\delta_T = K'$ that, according to (71), is equivalent to $K_T = K_T(V)$ (i.e., $\tau(T) = \alpha K_T$ or $\tau =$ const).

Then, by making use of identities (44), (71), (91), and (92), it can be proved that, if any two (except the pair (*1*) and (*3*)) of the four statements above hold true, then the other two statements are also valid. Moreover, then $\delta_T = K' =$ const and (44) always takes place. If, in addition to these two statements, it is assumed that $C_V =$ const or $C_V = C_V(T)$, then we have $\alpha = \alpha(V)$,
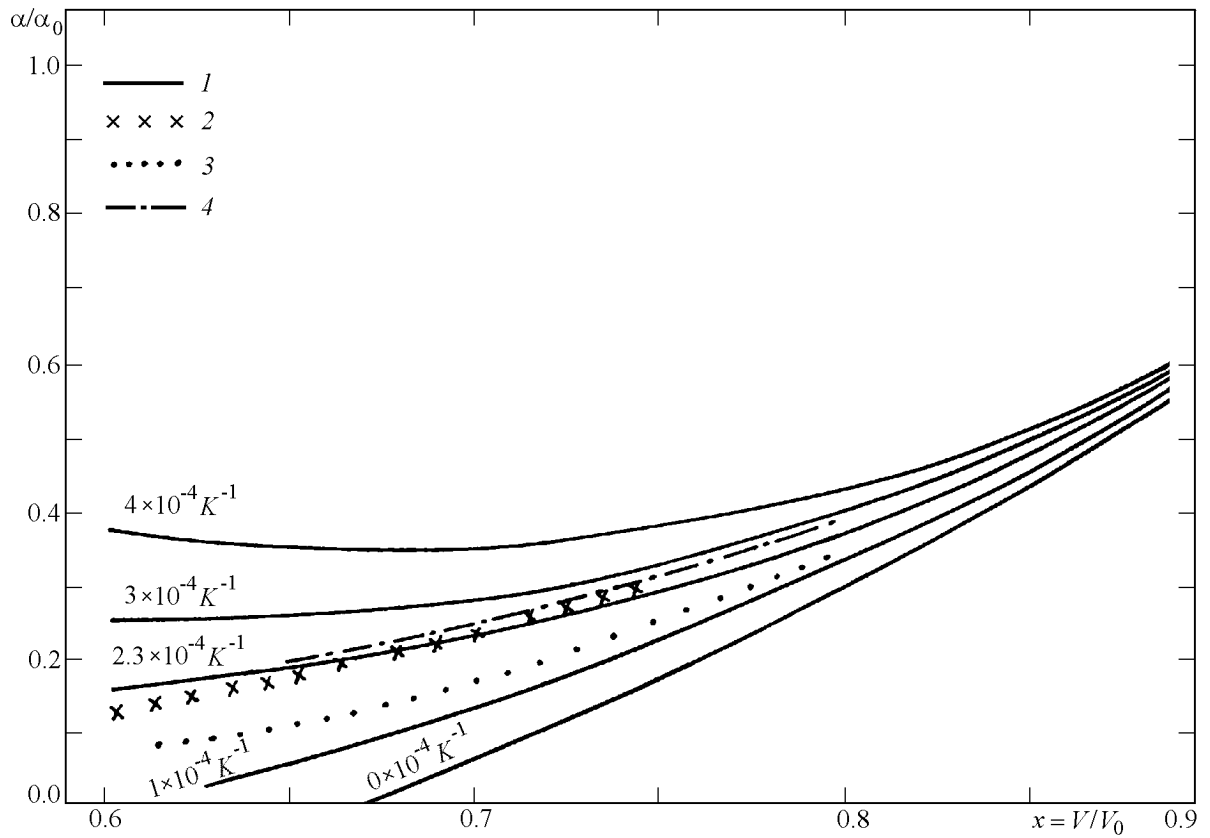
Figure 3. α/α_0 versus V/V_0 at $T = 1800$ K. (1) From (36)–(38) with allowance for the three first terms in (36) and with MgO parameters at 1800 K: $\alpha_0 = 5.13 \cdot 10^{-5}$ K^{-1}, $K_0 = 117$ GPa and $\delta_{T0} = 4.66$ from [*O. Anderson et al.*, 1992a] and $K_0' = 4.41$ (estimated under the condition that $d \ln K' / d \ln V = 1$ [*D. Anderson*, 1989]); shown at the curves are values of dK_0'/dT. (2) From (48) for $\delta_{T0} = 5$ and $k = 1.31$ [*O. Anderson et al.*, 1992b]. (3) $\alpha = \alpha_0 x^{\delta_T}$, where $\delta_T = 4.66$ [*O. Anderson*, 1967]. (4) From (47) for $\delta_{T0} = 4.66$ [*Chopelas and Boehler*, 1992]. The lower-mantle compression region is between $x = 0.85$ and $x = 0.70$ ($P/K_0 \approx 0.7$ at the base of the mantle, for $K_0 \approx 190 - 200$ GPa and $K_0' = 4$). Periclase (with $K_0 = 117$ GPa and $K_0' = 4.41$) is more compressible than the lower mantle, so that the third-order Birch–Murnagjan EOS for periclase yields $x \approx 0.65$ and $P/K_0 \approx 1.16$ for $P = 136$ GPa and $T = 1800$ K.

$K' = \delta_T = \hat{\alpha} = $ const and $\tau = $ const (see section 6.1 and (69) and (71)).

It is clear that such statements place constraints on the EOS formulation. For example, when an equation of type (28) is accepted instead of the Murnaghan EOS, only one of the above statements can strictly be true. Specifically, the concurrent use of the Birch–Murnaghan EOS and the assumption $\delta_T = \delta_T(T)$ (or $\delta_T = $ const) is incompatible with the condition $\delta_T = K'$ or $K' = K'(P)$.

Another not obvious inference is that the Murnaghan equation (44) uniquely follows from the assumptions $K_T = f(P) + aT$ (a being a constant) and $\tau = \tau(T)$ or const.

It is interesting to consider the use of the Murnaghan formula as the potential (lattice) part of the $P - V - T$ EOS in the classical high-temperature approximation. In general, for $C_V = $ const, we have a linear dependence of $K_T(V, T)$ on T (see (69) and (70)), and only for $\gamma/x = $ const ($q = 1$) and the Murnaghan potential, we obtain

$$K_T = aP + b + cT,$$

where a, b, and c are constants ($K' = $ const). Hence, it is seen that all isotherms ($T \geq 0$) are also represented by formula (44), but for a nonlinear $\gamma(x)$ behavior, this is, strictly speaking, not the case.

The consideration presented above concerns also the Birch's law, which for minerals with the mean atomic mass of $\mu = 20$–22 g/mole can be written in the power form $K_T = aV^b$ (where a and b are constants and the distinction between K_S and K_T is neglected). Since here $K' = $ const and $K_T = K_T(V)$ and (44) is used,

this law gives rise to $\delta_T = K' = $ const, formula (41), and for $C_V = $ const, $\alpha = \alpha(V)$.

Figure 1 shows the behavior α determined by (41), where the EOS is found by (37) with $K_0' = 3$ and 4 (the respective α curves pass through the ends of the bars in Figure 1).

The original assumption of *O. Anderson* [1967] δ_T = const was justified by the ultrasonic and shock-wave data of that time and was seemingly corroborated by later ultrasonic and resonance measurements [*O. Anderson et al.*, 1990; *Chopelas and Boehler*, 1992]. In particular, based on data for seven minerals, the value of $\delta_T = 4$–6 was recommended to be representative of the lower mantle. However, analyzing seismological and geoid data, *D. Anderson* [1987, 1989] found $\delta_T = 2$–3 for in situ lower-mantle conditions. The assumption can therefore be made that δ_T must decrease with pressure. Evidence for this can also be found in shock-wave and static compression data [*Birch*, 1986; *O. Anderson et al.*, 1993].

Ab initio calculations for MgO by *Reynard and Price* [1990] give a constant value in the range $0.7 \leq x \leq 1.0$. Another *ab initio* results [Isaak et al., 1990] reveal, however, that δ_T actually decreases by decreasing x.

To determine the $\alpha(x)$ more accurately than given by the power law (41), *Chopelas and Boehler* [1992] used data on the adiabatic pressure gradient τ_S and specific heat C_P. From the Maxwell relation (14), they derived

$$\delta_T = n + \left(\frac{\partial \ln C_P}{\partial \ln V}\right)_T - 1, \qquad (45)$$

where $n \equiv (\partial \ln \tau_S / \partial \ln V)_T$. Then, they set $n = mx$, where $m = 6 \pm 1$ from measurements for weakly compressible materials, and $(\partial \ln C_P / \partial \ln V)_T = 1$ or 0 for $T < \Theta$ or $T > \Theta$, respectively (compare with the data listed in Table 3 and the paper by *Pankov et al.* [1997]). Thus, the Chopelas and Boehler' formula for α can be written in the form

$$\frac{\alpha}{\alpha_0} = e^{\delta_{T0}(x-1)}, \quad \delta_T = mx, \text{ for } T < \Theta, \qquad (46)$$

$$\frac{\alpha}{\alpha_0} = \frac{1}{x} e^{(\delta_{T0}+1)(x-1)}, \quad \delta_T = mx - 1, \text{ for } T > \Theta. \quad (47)$$

O. Anderson et al. [1992a, 1992b, 1993] favored the power law $\delta_T = \delta_{T0} x^k$ (for $T \lessgtr \Theta$) that yields

$$\frac{\alpha}{\alpha_0} = e^{-\frac{\delta_{T0}}{k}(1-x^k)} \qquad (48)$$

with only small deviation from values by (47). The value of $k = 1.1$–1.4 in (48) was inferred from the theoretical PIB model of *Isaak et al.* [1990].

Applying (47) or (48) to the lower mantle, we find that α decreases 4–5 times along the "hot" lower-mantle adiabat, from the state $P = 0$ and $T \approx 1700$–2000 K to the base of the mantle. The power law (41) with $\delta_T = 5$–6 gives a greater decrease in α (6–8 times), and the same law with $\delta_T = 2$–3 results in a smaller decrease of α (2–3 times). Although approximations (47) and (48) are more preferable than (41), they require additional confirmation and information on parameters m, k, and $(\partial \ln C_P / \partial \ln V)_T$. For comparison, we note that the estimation of α in the lower mantle by (36) and (37), as described in section 6.2.1, with $dK_0'/dT = 2.3 \cdot 10^{-4}$ K^{-1}, gives the results close to those derived from (47) or (48) (Figure 3).

Similar results for α with δ_T decreasing under compression were obtained by *Zharkov* [1997] from his analysis of EOS's at extremely high pressures. Still earlier, *Zharkov* [1959] showed that the lower mantle thermodynamics quantified on the basis of the Debye model and seismic data gives the 4–5-fold decrease in α at the mantle base compared to the value at $P = 0$.

6.2.3. To this point, considering α at high compression, we have not applied to the Grüneisen parameter γ. However, the problem of thermal expansivity at high pressures and temperatures is intimately related to the problem of a similar variation of the Grüneisen parameter. *D. Anderson* [1987, 1989] characterized the lower-mantle thermodynamics by using the acoustic or Brilloin γ. For the adiabatic lower mantle, he found from PREM that $\gamma_0 = 1.4$ and $\alpha_0 = 3.8 \cdot 10^{-5}$ K^{-1} at $P = 0$ and $T = 1700$ K; the value of γ was determined by the thermodynamic relation (8) for $C_V = $ const $(T > \Theta)$. Given function $\gamma(V)$, the variation of α with volume in the classical temperature range can be evaluated by the formula derived from (8)

$$\frac{\alpha}{\alpha_0} = \frac{\gamma K_0}{\gamma_0 K_T x}. \qquad (49)$$

Note that the thermodynamic parameter γ, generally speaking, is different from the so-called lattice Grüneisen parameter [e.g., *Mulargia*, 1977; *D. Anderson*, 1989; *O. Anderson*, 1968, 1979b, 1980]. However, assuming that the latter depends only on volume, both parameters were found to coincide (the same inference follows from the quasiharmonic atomistic model of EOS at high temperatures, when, on the other hand, we come up with the purely thermodynamic consequence $\gamma = \gamma(V)$ for $C_V = $ const (see section 11).

The three most familiar formulas for the lattice γ can be written in the general form [*Zharkov and Kalinin*, 1971]

$$\gamma = \frac{9K' + 2mP/K_T - 6m - 3}{6(3 - 2mP/K_T)}, \qquad (50)$$

where $m = 0$, 1, or 2 gives the formulas of Slater,

Dugdale–Macdonald, and Zubarev–Vashcheno (or *Irvine and Stacey* [1975]), respectively. The latter of these formulas appears to be the most favored, at least at $T > \Theta$, for high symmetry crystals. Following *Leibfried and Ludwig*, 1961], γ can approximately be expressed in terms of the root-mean-square frequency of atomic oscillations. For cubic crystals with the central interaction, when only the nearest neighbors are allowed for, this approximation also leads to the Zubarev–Vashchenko formula [*Pankov,* 1983; *Hofmeister,* 1991a].

Calculation by (50) requires knowledge of the $P(V)$ dependence at $T = 0$ K, but the replacement of the $T = 0$ K isotherm by any isotherm at $T > 0$ K is not significant for this case. Using the EOS from (37) at $K'_0 = 4$ and determining γ by (50) at $m = 2$ and then α by (49), we obtain $\alpha_0/\alpha = 1.7$ for $x = 0.7$ (that is approximately at the mantle base). Such a small decrease in α compared to the 4–5-fold decrease found above is due to the fact that the EOS by (37), like many other $P(V)$ relationships [*Pankov and Ullmann,* 1979b], results in a low value of the slope

$$q \equiv \left(\frac{\partial \ln \gamma}{\partial \ln x}\right) \sim 0 - 0.5,$$

calculated from (50). This either tells us that a more flexible EOS involving the independent parameter $K_0 K''_0 \equiv K_2$ (such as in model 2 by *Ullmann and Pankov* [1980] or the Birch–Murnaghan fourth-order EOS) must be introduced, or some amendments to (50) are required. The Zubarev–Vashchenko formula was somewhat improved by *Stacey* [1981, 1992], but nevertheless, the slope q for most two-parametric (K_0 and K'_0) EOS's appears to remain low).

Another useful approximation for γ is the empirical power law [e.g., *O. Anderson,* 1968, 1974; *McQueen et al.,* 1970]

$$\gamma = \gamma_0 x^q, \tag{51}$$

where q is often assumed to be one, according to shock-wave data [*McQueen,* 1991] or studies of the mantle [*O. Anderson,* 1979b; *D. Anderson,* 1989]. From (49) with $q = 1$, we find Birch's formula $\alpha K_T = \alpha_0 K_0 = $ const, which gives $\alpha_0/\alpha = 3.5$–4.0 at the mantle base (for $x = 0.7$, $K'_0 = 4$, $K_T/K_0 = 3.51$, and $T = 2000$–3000 K). The value of $q = 1.5$–2.0 may be more favored for the mantle perovskite [*Pankov et al.,* 1998], yielding, however, $\alpha_0/\alpha = 4.2$–5.0 that is close to the result obtained from (47) and (48).

Note that, according to (49), the assumption of the power laws for α (41) and γ (51) again gives the Murnaghan EOS (44). Since the latter fits data well over a range of $P/K_0 \lesssim 0.3$ ($x \lesssim 0.82$), we expect (41) to be a sufficient approximation for α in the same compression range.

Duffy and Ahrens [1993] estimated α from shock wave data for MgO, CaO, CaMgSi$_2$O$_6$ and ε–Fe at pressures to $P > 140$ GPa. By using (49) and (51) with $q = $ const and K_T/K_0 from the PIB model for MgO [*Isaak et al.,* 1990], they found $q = 0.5 \pm 0.5$ that is smaller than $q = 0.83$–1.26 in the compression range $x = 0.67$–1.0 along the PIB isotherm. Periclase is more compressible than the lower mantle matter and has $x = 0.67$ at $P = 134$ GPa near the mantle base (according to the PIB 2000 K isotherm of MgO, $P/K_0 = 1.047$, $K_T/K_0 = 4.699$, and $K' = 4.74$). With these values, the shock wave results of Duffy and Ahrens for MgO give $\alpha_0/\alpha = 3.1$–4.7 at the mantle base ($x = 0.67$), i.e., the value 1–1.6 times less than α_0/α by (47) and (48) at the typical value of $\delta_{T0} = 5 \pm 1$ (if the value $\delta_{T0} = 4$ is used in (47) and (48), the resulting α_0/α value will be closer to the shock-wave estimate above). These results can be viewed as an argument for the decrease of both δ_T and q under compression.

In analysis of the volume dependence of γ, *O. Anderson et al.* [1993] proposed the power law

$$q = q_0 x^\nu, \tag{52}$$

which, similarly to (48), yields

$$\frac{\gamma}{\gamma_0} = e^{-\frac{q_0}{\nu}\left(1 - x^\nu\right)}. \tag{53}$$

Setting $q_0 = 1.5$–2.0 and $\nu = 1$ (as for MgO, according to *O. Anderson et al.* [1992b]), we find from (49) that $\alpha_0/\alpha = 4$–4.5 at $x = 0.7$. Note that q_0 for MgO descends from 1.72 to 1.26 as temperature increases from 300 K to 2000 K [*O. Anderson et al.,* 1993].

In total, many estimates of α_0/α using various methods described above consistently show that the thermal expansion coefficient in the lower mantle decreases 4–5 times along the hot low-mantle adiabat as the pressure increases from zero to the base of the mantle. Nevertheless, the complete consensus on all the parameter values related to these estimates (e.g., for q and δ_T) has yet not been achieved.

6.3. Temperature dependence of α at $P = 0$

6.3.1. Most data on thermal expansion refers to the dependence $\alpha(T) = \alpha_0$ at $P = 0$. The value of α_0 is necessary, in particular, to extrapolate the thermal expansivity data to higher pressures in the mantle. The typical behavior of $\alpha(T)$ is illustrated in Figures 4 and 5. Usually, the data at $P = 0$ are fitted using the empirical formula [e.g., *Fei et al.,* 1990, 1991]

$$\alpha = a_0 + a_1 T + a_2 T^{-2}, \tag{54}$$

which we used to calculate α presented in Table 2 (and in *Pankov et al.* [1997]). Note that the applicability

of (54) can also be justified by calculations of phase diagrams [*Fei et al.*, 1990, 1991].

A theoretically based approach to calculating $\alpha(T)$ was developed by *Suzuki* [1975a, 1975b], who used the Mie–Grüneisen EOS yielding

$$\alpha = \left(\frac{\partial E_t}{\partial T}\right)_P \left[Q^2 \left(1 + \frac{E_t}{Q} - \frac{kE_t}{Q}\right)\left(1 - \frac{kE_t}{Q}\right)\right]^{-1}, \quad (55)$$

where E_t is the Debye thermal energy

$$E_t = \frac{3R}{\mu}D(z), \ z = \Theta/T, \ D(z) = \frac{3}{z^3}\int_0^z \frac{y^3\,dy}{e^y - 1},$$

$k = \frac{1}{2}(K_0' - 1)$, $Q = \frac{K_0 V_0}{\gamma}$, and $D(z)$ is the Debye function. Here, it is assumed that $\gamma = $ constant, and parameters K_0 and K_0' are defined at $T = 0$. The fitted parameters are Q, k, and Θ. Formula (55) is derived by expanding the potential pressure in V and truncating at only two first terms. The Θ values obtained from this method are given in Table 2 (see also *Pankov et al.* [1997]).

O. Anderson et al. [1992a] extrapolated $\alpha_0(T)$ from a fixed value at $T^* > \Theta$ to higher temperature using the relation

$$\frac{\alpha_0(T)}{\alpha_0(T^*)} = \frac{1}{1 - \alpha_0(T^*) \cdot \delta_T \cdot (T - T^*)}, \quad (56)$$

where $\delta_T = \hat{\alpha} = $ constant (see (32)). Formula (56) is easily derived from the condition that α_0 at $P = 0$ varies with density by the power law. Note that (56) has an asymptote close to which α dramatically increase with temperature (reflecting to some extent the fact that the potential energy has an inflection point).

6.3.2. For a more complete consideration of the temperature behavior of α, we calculated $\alpha(T)$ for three minerals from the Mie–Grüneisen EOS (with the Debye model), in which, unlike the Suzuki method, $\gamma(x)$ was found by (51) with $q = 0$, 1, and 2, and room-temperature isotherms were represented by equations (28) and (37). The material parameters of the EOS's were found from values of ρ, K_S, α, C_P, and $(\partial K_S/\partial P)_T$ at normal conditions (Tables 2 and 3).

The results of the computations are shown by the solid lines in Figures 4 and 5. We see that the curves for periclase and particularly forsterite systematically deviate from the experimental points at high temperatures, although there is a considerable uncertainty in data for α at high temperatures. Nevertheless, such deviations can be caused by the fact that the temperature dependence of γ (at $V = $ const) is not accounted for in the Mie–Grüneisen EOS [*Mulargia*, 1977; *Mulargia and Boschi*, 1980; *Mulargia et al.*, 1984; *O. Anderson*

et al., 1992a; *Molodets*, 1998]. To gain a better insight into the quality of the Mie–Grüneisen EOS and to construct a self-consistent database on EOS parameters, it is very important to measure the thermal expansivity of minerals at high temperatures, up to their melting points. This conclusion was emphasized by many authors [e.g., *Saxena*, 1988, 1989; *Goto et al.*, 1989; *Isaak et al.*, 1989b; *Gillet et al.*, 1991; *Richet et al.*, 1992].

7. Specific Heat

The lattice specific heat of minerals at $T \gtrsim 1000$ K is close to the classic limit $3Rn = 3RM/\mu$ (the molar value, where R is the gas constant and n is the number of atoms in chemical formula). From calorimetry, we have information on the isobaric heat capacity C_P, which exceeds C_V by 1–3% at 300 K and 10–15% at $T > \Theta$ (Table 2 and *Pankov et al.*, 1997]. Since $\mu \approx$ 20–22 g/mole for mantle minerals, the classic value of C_V for them is 1.13–1.25 J/g K. Depending on mineral, the high-temperature anharmonic corrections to C_V become singnificant either near the melting point or even at room temperature (sometimes, at T equal 1/6 of the melting point) [*Mulargia and Boschi*, 1980; *Quareni and Mulargia*, 1988; *Reynard et al.*, 1992; *Fiquet et al.*, 1992].

7.1. *P–V–T* derivatives of specific heat

From the identities $\partial^2 E/\partial V \partial T = \partial^2 E/\partial T \partial V$ and $\partial^2 S/\partial P \partial T = \partial^2 S/\partial T \partial P$, using the Maxwell relations, we find

$$\left(\frac{\partial C_V}{\partial P}\right)_T = -\frac{VT}{K_T}\left(\frac{\partial \alpha K_T}{\partial T}\right)_V, \quad (57)$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P = -\alpha^2 VT(1 + \hat{\alpha}). \quad (58)$$

Note that (57) and (58) are the alternate forms of (33) and (34), repectively. The logarithmic volume derivatives at $T = $ constant can be expressed as follows:

$$\left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T = \alpha\gamma T[\hat{\alpha} - 2\delta_T + K'], \quad (59)$$

$$\left(\frac{\partial \ln C_P}{\partial \ln V}\right)_T = \alpha\gamma T(1 + \alpha\gamma T)^{-1}(1 + \hat{\alpha}). \quad (60)$$

These identities were used to compute the derivative values given in Tables 3 and in *Pankov et al.* [1997]. *O. Anderson et al.* [1993] noted that, for the Debye model, $(\partial C_V/\partial P)_T \lesssim 0$ and therefore $\hat{\alpha} \gtrsim 2\delta_T - K'$.

The difference $C_P - C_V$ satisfies the identity

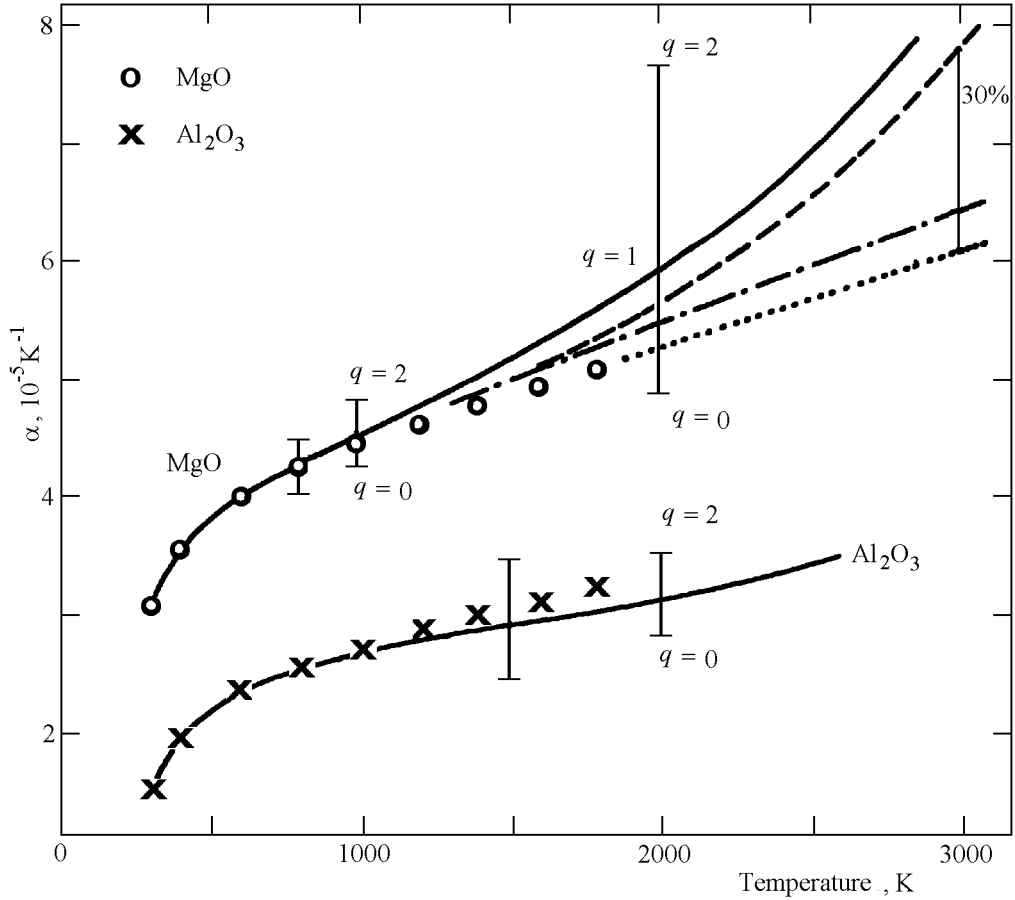$$\frac{1}{\alpha^2 VT}\left(\frac{\partial(C_P - C_V)}{\partial P}\right)_T = K' - 2\delta_T - 1, \quad (61)$$

Figure 4. Temperature dependence of the thermal expansion coefficient at $P = 0$ for MgO and
Al$_2$O$_3$. The solid lines are from the Mie–Grüneisen EOS with $q = 1$; the bars show deviations
for $q = 0$ and 2, respectively. A simple linear extrapolation of α is shown by points. The dashed
line is α by (56) for $T_0 = 1000$ K and $\delta_{T0} = 4.84$. The dot-and-dash line is α by (54) [*Fei et al.*,
1990]. The experimental points (circles for MgO and crosses for Al$_2$O$_3$) are from *O. Anderson et
al.* [1992a].

i.e., it decreases with pressure for usual values of K' and
δ_T (see Table 3 and *Pankov et al.* [1997]).

Birch [1952] estimated the decrease in C_P with pressure in the lower mantle, setting $\hat{\alpha} \sim 4$ and $\alpha\gamma T \sim 0.1$.
By the power law for C_P, this gives a 13–16% decrease
in C_P along an isotherm, for x descending from 1.0 to
0.7. According to Birch, the maximum decrease in C_P
in the mantle does not appear to exceed 20%.

The adiabatic volume derivative of C_P is

$$\left(\frac{\partial \ln C_P}{\partial \ln V}\right)_S = -\gamma \left(\frac{\partial \ln C_P}{\partial \ln T}\right)_S$$

$$= (1 + \alpha\gamma T)\left(\frac{\partial \ln C_P}{\partial \ln V}\right)_T - \gamma \left(\frac{\partial \ln C_P}{\partial \ln T}\right)_P. \quad (62)$$

Substituting $(\partial \ln C_P/\partial \ln T)_P \sim 0.15$ (the typical
value for minerals for $T \gtrsim 1000$ K), $\gamma \sim 1 - 1.5$, $\alpha\gamma T \sim$

0.1, and $(\partial \ln C_P/\partial \ln V)_T \sim 0.5$ (for $\hat{\alpha} \sim 4$), we find
$(\partial \ln C_P/\partial \ln V)_S \approx 0.3 - 0.4$. Consequently, the power
law for C_P yields a 8–13% decrease of this value along
the mantle adiabat (to $x \sim 0.7$).

By using (29), the temperature derivative of C_P can
be represented in the form

$$\left(\frac{\partial \ln C_P}{\partial \ln T}\right)_P$$

$$= \left(\frac{\partial \ln C_P}{\partial \ln T}\right)_V + \frac{\alpha\gamma T}{\gamma}\left(\frac{\partial \ln C_P}{\partial \ln V}\right)_T, \quad (63)$$

The second term arising from the extrinsic anharmonicity can be estimated by making use of (58), so that
(63) in conjuction with data for $(\partial C_P/\partial T)_P$ allows the
first term coming from the intrinsic anharmonicity to
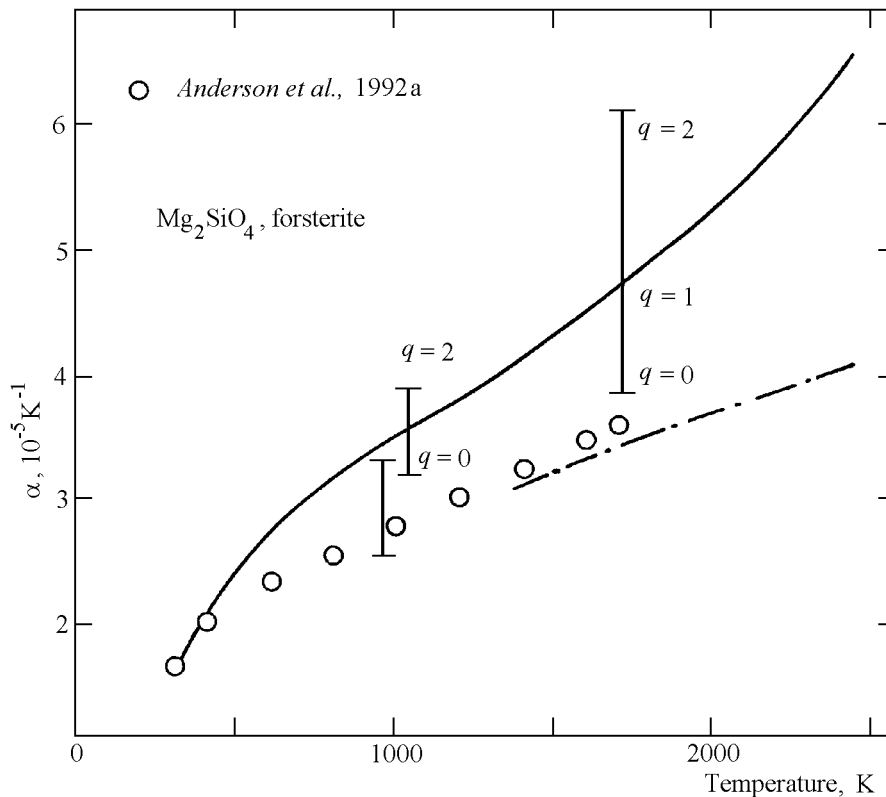be evaluated. At room temperature, $(\partial \ln C_P/\partial \ln V)_T$

Figure 5. Temperature dependence of the thermal expansion coefficient at $P = 0$ for forsterite. For notation, see Figure 4.

is on the order of $(\partial \ln C_P / \partial \ln T)_P$, but nevertheless, the contribution of the second term to the sum (63) is small because of the small factor $\alpha \gamma T$. At high temperatures, this contribution generally increases to 15–30% (perhaps, 60–70% for ilmenite and perovskite, according to our estimates) [*Pankov et al.*, 1997]. In the classical limit, $C_V = $ constant, assuming that $\alpha \approx \alpha(V)$ and $\gamma \approx \gamma(V)$, we find $(\partial C_P / \partial T)_V \approx \alpha \gamma C_V$.

Further, from (17) and (18), it is easy to obtain the identity

$$\left(\frac{\partial \ln C_V}{\partial \ln T} \right)_P = \frac{T}{C_V} \left(\frac{\partial C_P}{\partial T} \right)_P$$

$$-\alpha \gamma T - \frac{(\alpha \gamma T)^2}{\gamma} \left(1 + 2\hat{\alpha} - \delta_T \right), \quad (64)$$

which we used to estimate the values of this derivative presented in Table 3 and *Pankov et al.* [1997]. Then, with the help of the identity

$$\left(\frac{\partial \ln C_V}{\partial \ln T} \right)_P = \left(\frac{\partial \ln C_V}{\partial \ln T} \right)_V + \frac{\alpha \gamma T}{\gamma} \left(\frac{\partial \ln C_V}{\partial \ln V} \right)_T \quad (65)$$

it is possible to compute $((\partial \ln C_V)/(\partial \ln T))_V$, provided that the second term in (65) is given by (59).

An explicit dependence $C_V(V, T)$ can be derived from models and measurements of the vibrational spectra of solids (e.g., *Pitzer and Brewer,* 1961]):

$$C_V = 3nk \int\limits_0^\infty \frac{e^y y^2}{(e^y - 1)^2} g(\nu) d\nu, \quad (66)$$

where k is the Boltzman constant, $y = h\nu/kT$, $g(\nu)$ is the spectrum density, and ν are the lattice frequencies including optic and acoustic modes [*Kieffer,* 1979a, 1979b, 1979c, 1980; *Hofmeister,* 1991a, 1991b; *Richet et al.,* 1992]. This method provides information on the inadequacy of the Debye theory and the related approximation $\gamma = -d \ln \Theta / d \ln V$. The characteristic temperature Θ in the Debye theory is usually estimated from acoustic data, but Θ found from data for C_V at $T \geq$ 300 K (labelled Θ_{th}), on average, exceeds the acoustic Θ (labelled Θ_a) by about 20% (larger deviations are common to quartz and coesite, see Table 2 and *Pankov et al.* [1997] and *Watanabe* [1982]). *Chopelas* [1990b] found, however, good agreement of the Debye model with the spectrum data for MgO at pressures to 200 kbar, provided that $\Theta \approx V^\gamma$, i.e., $q = 0$.

Spectroscopic measurements at high pressures allow us to estimate the derivative $(\partial C_V / \partial P)_T$. For example,

the data of *Chopelas* [1990a, 1990b] to 200 kbar show that C_V linearly decreases with P, so that the gradient $-(\partial C_V/\partial P)_T$ is $17.6 \cdot 10^{-3}$ ($T = 300$ K) and $0.91 \cdot 10^{-3}$ ($T = 1800$ K) for MgO and $49.8 \cdot 10^{-3}$ ($T = 300$ K) and $3.4 \cdot 10^{-3}$ ($T = 1800$ K) J/(mole K kbar) for forsterite. With these values, C_V being extrapolated (by the power volume dependence) to the maximum pressure $P = 1357$ kbar in the mantle will decrease 40–60, 8–12, and 2–3% on the 300, 1000, and 1700 K isotherms, respectively. Comparing these results with the decrease in C_P estimated above, we verify that the difference $C_P - C_V$ in the lower mantle must be exceedingly small. From the same Chopelas' data, using also the K_T and C_V values from Table 2, we find $(\partial \ln C_V/\partial \ln V)_T = 0.77$ ($T = 300$ K) and 0.022 ($T = 1800$ K) for MgO and 0.54 ($T = 300$ K) and 0.022 ($T = 1700$ K) for forsterite. These results are comparable to our estimates of this derivative from thermodynamic data (Table 3).

7.2. An explicit temperature dependence of C_P at $P = 0$

Calorimetric data for C_P versus temperature at $P = 0$ are commonly fitted to various empirical expressions [e.g., *Fei and Saxena*, 1987; *Berman*, 1988; *Saxena*, 1989; *Richet and Fiquet*, 1991]:

$$C_P = C_0 + C_1 T + C_2 T^2 + C_3 T^{-1/2} + C_4 T^{-2},$$
$$C_P = C_0 + C_1 T^{-1/2} + C_2 T^{-2} + C_3 T^{-3},$$
$$C_P = C_0 + C_1 T^{-1} + C_2 T^{-2} + C_3 T^{-3} + C_4 T, \quad (67)$$
$$C_P = C_0 + C_2 T^{-2} + C_4 T^{-4} + C_6 T^{-6},$$
$$C_P = C_0 + C_1 T^{-1} + C_2 T^{-2} + C_3 T^{-3} + C_4 \ln T.$$

Richet and Fiquet [1991] showed that the last of the above formulas are favored but no one of them provides an accurate description of C_P over a wide temperature range.

In addition, Figure 6 compares $C_P(T)$ found by the simpler formula used by *Watanabe* [1982] to fit the measurement in the temperature interval of 350–700 K. An example of MgO shows that the extrapolation by this formula can lead to series errors.

As well as in the analysis of thermal expansivity in section 6.3, we calculated $C_P(T)$ (Figure 6) from the same Mie–Grüneisen EOS as was used to compute α. One can see that the theoretical curves can be reconciled with the data shown by varying parameter q in the limits 1–2. In so doing, we find $q \approx 0$ for MgO, $q = 1–2$ for Al$_2$O$_3$, and $q \approx 0.5$ for forsterite. However, these values of q are not always consistent to data on α (see section 6.3), and this fact also suggests a certain inaccuracy of the Mie–Grüneisen EOS model.

8. Thermal Pressure

8.1. P–V–T derivatives of the thermal pressure coefficient

The thermal pressure coefficient defined by (9) or (12) is the basic characteristic of the thermal pressure and can also be defined as $\tau = (\partial P_{th}/\partial T)_V$. Note that τ has also the meaning of the latent heat of expansion per 1 K. O. Anderson and his co-workers [*O. Anderson*, 1982, 1984, 1988; *O. Anderson and Sumino*, 1980; *O. Anderson and Goto*, 1989; *O. Anderson et al.*, 1982, 1991, 1992a] paid special attention to this parameter, in particular, in relation to their development of the rectangular parallelepiped resonance technique for measuring elastic properties of minerals at high temperatures.

The basic identities for the derivatives of τ can easily be derived from those given in sections 6 and 7. The following identities are especially suitable [*Brennan and Stacey*, 1979; *Birch*, 1978; *O. Anderson and Yamamoto*, 1987]:

$$\left(\frac{\partial \alpha K_T}{\partial T}\right)_P = K_T \left(\frac{\partial \alpha}{\partial T}\right)_V = \alpha^2 K_T \left(\hat{\alpha} - \delta_T\right), \quad (68)$$

$$\left(\frac{\partial \alpha K_T}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial C_V}{\partial V}\right)_T$$
$$= \alpha^2 K_T \left(\hat{\alpha} + K' - 2\delta_T\right), \quad (69)$$

$$\left(\frac{\partial \alpha K_T}{\partial V}\right)_T = -\frac{1}{V} \left(\frac{\partial K_T}{\partial T}\right)_V, \quad (70)$$

$$\left(\frac{\partial \alpha K_T}{\partial P}\right)_T = \frac{1}{K_T} \left(\frac{\partial K_T}{\partial T}\right)_V = \alpha \left(K' - \delta_T\right). \quad (71)$$

Formula (68) is obtained by expanding the derivative at the left side and then by using (30); (69) is a consequence of (57), and (70) is easily derived by equating the second derivatives of P with respect to V and T taken in one order or another; finally, (71) follows from (31) and (70).

Combining (68) and (69), we have

$$\left(\frac{\partial \alpha K_T}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial C_V}{\partial V}\right)_T - \alpha^2 K_T \left(K' - \delta_T\right). \quad (72)$$

According to (71), for the common inequality $\delta_T > K'$, parameter τ decreases with pressure along an isotherm. However, at high pressure, the decrease can change to an increase, as, e.g., in the PIB model for MgO [*O. Anderson et al.*, 1993]. It is clear from (68)
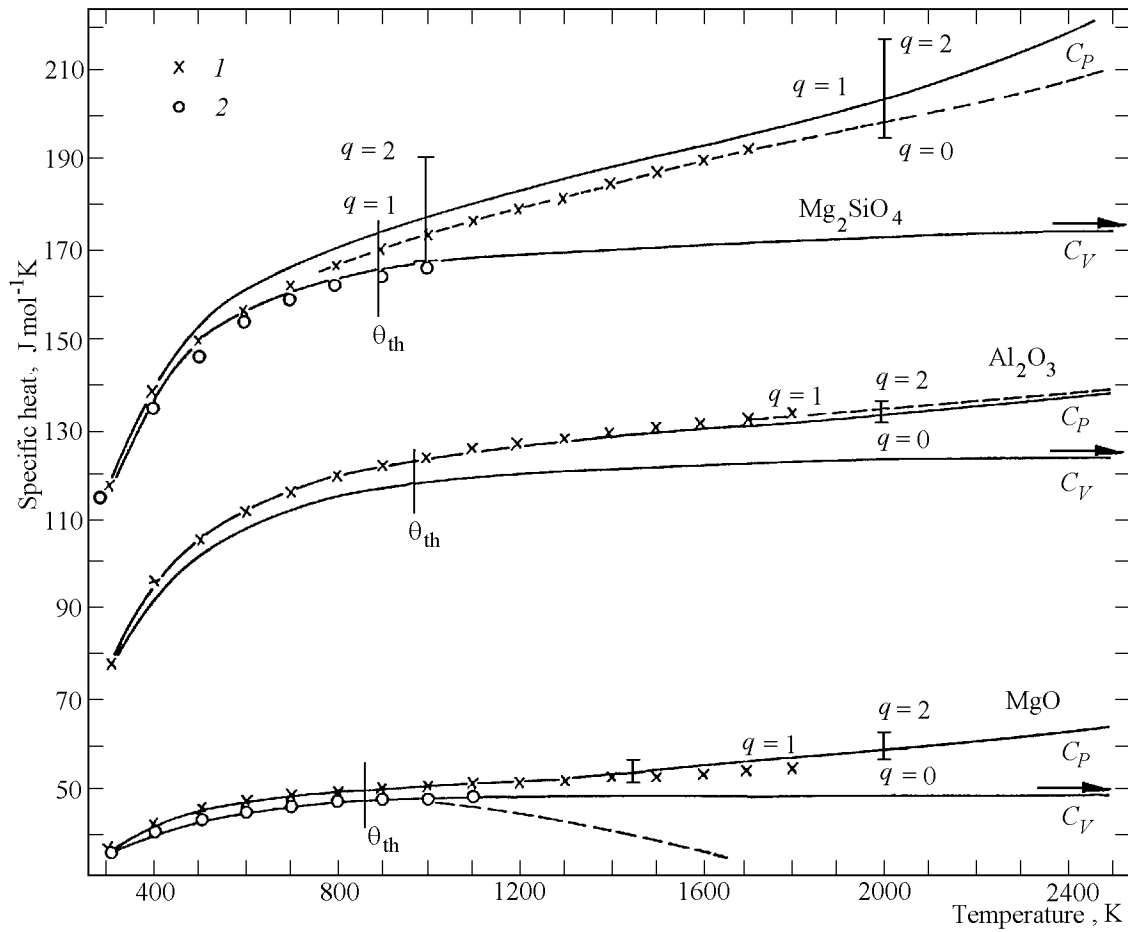
Figure 6. Temperature dependence of the specific heat at $P = 0$ for forsterite, corundum, and periclase. (1) C_P from [*O. Anderson et al.*, 1992a]. (2) C_V from [*Chopelas*, 1990a, 1990b]. The solid lines are from the Mie–Grüneisen EOS (with the same parameter values for respective minerals as in Figures 4 and 5). The dashed lines are the polynomials from [*Watanabe*, 1982] descrbing his data in the range 350–700 K. The arrows indicate the classical values of C_V.

that τ increases with temperature at constant pressure, at least for $T < \Theta$.

As follows from (29), the logarithmic temperature derivative of τ at $P = $ constant is represented as

$$\left(\frac{\partial \ln \tau}{\partial \ln T}\right)_P = \frac{1}{\alpha}\left(\frac{\partial \ln \tau}{\partial T}\right)_V + \left(\frac{\partial \ln \tau}{\partial \ln V}\right)_T, \quad (73)$$

where the first, intrinsic anharmonic term is positive due to (69) and can be written as the sum of two terms

$$\frac{1}{\alpha}\left(\frac{\partial \ln \tau}{\partial T}\right)_V$$

$$= \frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_V + \frac{1}{\alpha^2}\left(\frac{\partial \alpha}{\partial T}\right)_V \quad (74)$$

$$= (K' - \delta_T) + (\hat{\alpha} - \delta_T),$$

and the second term in (73), in view of (70) and (71), is

$$\left(\frac{\partial \ln \tau}{\partial \ln V}\right)_T = \delta_T - K'$$

$$= -\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_V \equiv -\delta_V^T \quad (75)$$

Here, the symbol δ_V^T is introduced for convenience (see a further analysis in section 9). Although due to large values of $\hat{\alpha}$, the intrinsic anharmonic term in (73) is dominant in value at $T < \Theta$, the sign of (73) at high temperatures can be either positive or negative.

The temperature behavior of τ resembles that of C_V, so that at $T > \Theta$, τ tends to be independent of temperature [*O. Anderson*, 1984]. Accordingly, the thermal pressure P_{th} tends to a linear dependence on T. Our estimates of τ (Table 2 and *Pankov et al.* [1997]) show that the nonlinear terms in P_{th} versus T makes a con-

tribution not greater than 1–3% at the highest temperatures indicated in Table 3 and *Pankov et al.* [1997]. The linear temperature behavior of P_{th} is considered to be the universal property of solids at high temperatures [*O. Anderson et al.*, 1992a]. Unlike the temperature dependence, the extent to which τ depends on volume at $T =$ constant varies from one type of solid to another. According to *O. Anderson et al.* [1992a], the earth minerals fall into an intermediate group between materials with significant (e.g., gold) and relatively weak (e.g., sodium chloride, alkali metals, noble elements) volume dependences of τ. It is important that these inferences are based on both $P-V-T$ data (analysis of $P_{th}(V,T)$) and high-temperature data for K_T and αK_T at $P = 0$ (analysis of (70)).

At first glance, the observed regularity in $\tau(T)$ at $T > \Theta$ is explained by the fact that $C_V \approx$ constant in this temperature range, where, in view of (8) and (69), γ is therefore independent of temperature. In other words, the quasiharmonic Mie–Grüneisen EOS is seemingly justified at high temperatures. However, this is not quite true to be the general case when we start with the condition $\tau =$ constant or $\tau = \tau(V)$ which are compatible with the case of $C_V(T)$ (see (69)) and therefore with a dependence of γ on both volume and temperature [*O. Anderson and Yamamoto,* 1987]. Theoretically, the departure of C_V from the Dulong and Petit law [e,g., *Mulargia and Broccio,* 1983; *O. Anderson and Suzuki,* 1983; *Gillet et al.,* 1991; *Reynard et al.,* 1992] is in part related to the intrinsic anharmonicity described by the third and higher order terms in the lattice Hamiltonian expansion. In describing experimental data, the thermal EOS generally requires smaller number of terms in this expansion than the caloric EOS [*Leibfried and Ludwig,* 1961; *Wallace,* 1972; *Davies,* 1973]. Thus, when anharmonicity in P_{th} versus T and the temperature dependence of γ are not observed, this may suggest that either the quasiharmonic limit for the vabrational γ has not yet been achieved or the higher order terms in the thermal part of the EOS are mutually cancelled [*O. Anderson et al.,* 1982].

In conclusion to the above analysis of τ, we formulate the following important assumptions and their consequences that can easily be verified: (1) Let C_V be independent of V, i.e., either $C_V = C_V(T)$ or $C_V =$ constant. (2) Assume that $K_T = K_T(V)$ that is equivalent to $\delta_T = K'$. From (1), it follows that either $\tau = \tau(V)$ or $\tau =$ constant, and in addition, K_T is either a linear function of T or $K_T(V)$, which leads to $q = q(V)$ (or $q = 1$) and either $\gamma = V\tau(V)/C_V(T)$ or $\gamma = \gamma(V)$. The statement (2) is equivalent to either $\tau = \tau(T)$ or $\tau =$ constant. If both (1) and (2) statements are valid (but $C_V \neq$ constant), then $\gamma =$ const $\cdot V/C_V(T)$ and $q = 1$. The conditions $C_V =$ constant and $K_T = K_T(V)$ yield $\gamma =$ const $\cdot V$.

8.2. Thermal pressure model

The thermal EOS resulting directly from integrating (12) is of the form

$$P = f(V) + \int_0^T \alpha K_T dT = f(V) + \int_0^T \gamma \frac{C_V}{V} dT, \quad (76)$$

where $f(V)$ is the static lattice pressure plus the zero oscillation pressure. The second term in (76) is the total thermal pressure P_{th} accounting for all anharmonic contributions. This EOS can be rewritten in the form

$$P = P(V, T_0) + \int_{T_0}^T \alpha K_T dT, \quad (77)$$

where, for example, $T_0 = 300$ K. In accordance with the behavior of τ described above, the thermal pressure can be approximated as [*O. Anderson,* 1984, 1988]

$$P_{th} = \int_0^{T_1} \alpha K_T dT + \int_{T_1}^T \alpha K_T dT$$

$$= a(V) + b(V)(T - T_1), \quad (78)$$

where $T \geq T_1 \geq \Theta$. As already noted, the variation with volume in (78) is insignificant for some solids.

In the Mie–Grüneisen EOS, the thermal pressure is however defined as

$$P_{th} = \frac{\gamma(V)}{V} \int_0^T C_V dT, \quad (79)$$

where the quasiharmonic approximation for C_V is used. Thus, here, at high temperatures $T \geq T_2 \geq \Theta$, when $C_V \approx$ constant,

$$P_{th} = a^*(V) + b^*(V)(T - T_2). \quad (80)$$

Even when $b(V) = b^*(V)$ in some temperature range, the distinction between (78) and (80) is retained since, in the general case, $\gamma = \gamma(V, T)$ in (78) and $a^* \neq a$. In practice, for certain minerals and for the present accuracy of measurements, P_{th} from (78) and the Mie–Grüneisen theory can be indistinguishable [*Fei et al.,* 1992a, 1992b; *Mao et al.,* 1991], especially for minerals with low Debye Temperature.

The term ΔP_{th} in (77) can be approximated in various ways. For example, with given volume dependences of K' and δ_T, by integrating (75), we can find $\tau(V)$ at $T =$ constant [*O. Anderson et al.,* 1992a, 1993]. The temperature dependence of τ is derived from data on
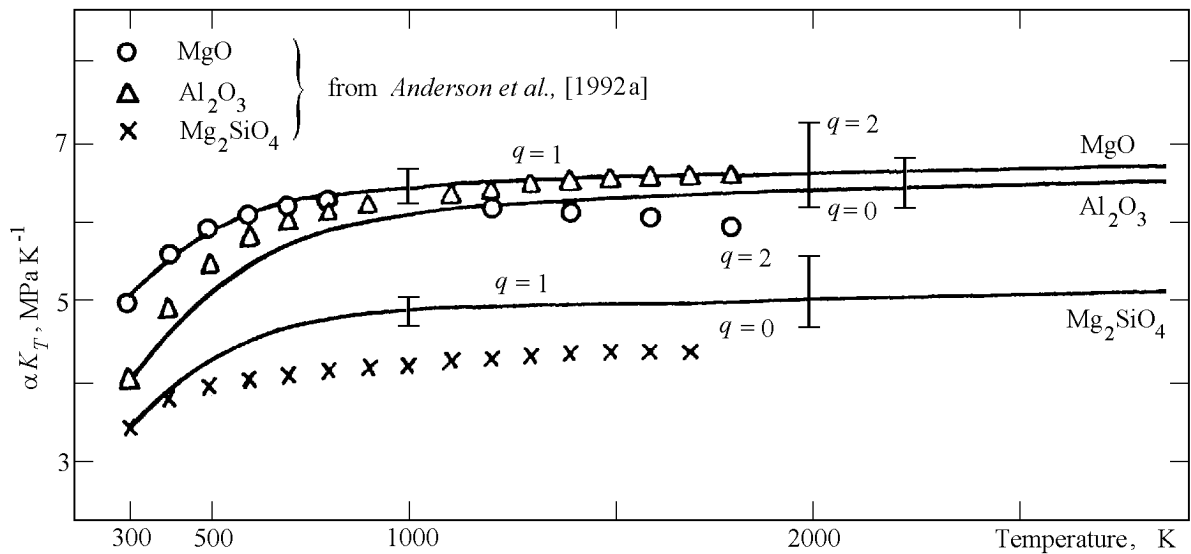
Figure 7. Thermal pressure coefficient versus temperature at $P = 0$. The solid lines are from the Mie–Grüneisen EOS (as in Figures 4–6). The experimental points are from [*O. Anderson et al.*, 1992a].

$\alpha(T)$ and $K_T(T)$ at $P = 0$. Another possibility to explicitly approximate the thermal pressure is given by the power law for $\tau(V)$ on an isotherm.

Fei et al. [1992a, 1992b] and *Mao et al.* [1991] used a number of models for P_{th} in order to describe $P - V - T$ X-ray data. Specifically, they assumed $(\partial K_T/\partial T)_V = $ constant. Then, (70) yields

$$\tau(P,T) = \tau(0,T) + \left(\frac{\partial K_T}{\partial T}\right)_V \ln \frac{V(P,T)}{V(0,T)}, \qquad (81)$$

where $\tau(0,T)$ is determined from data on α provided that $(dK_T/dT)_P = $ constant, the condition assumed over the entire $P - V - T$ range of measurements. From the assumption that both temperature derivatives of K_T are constant, it follows that $\tau K' = $ const. However, in such a case, K' will increase with pressure along an isotherm and decrease with temperature along an isobar—the behavior that disagrees with the usual properties of this parameters (see section 6). Note that the estimated δ_T values can be very sensitive to the adopted model of P_{th} [e.g., *Mao et al.*, 1991], although the P_{th} values themselves from various models can be close.

Finally, in Figure 7, we illustrate the temperature dependences of τ at $P = 0$, calculated from the Mie–Grüneisen EOS for periclase, corundum, and forsterite, described in section 6, with various values of q in the interval 0–2. Although this type EOS gives correct orders of magnitude and the correct regularities in the $P - T$ variations of τ, it is difficult to achieve the complete consistency for all of the data given, as well as in the

cases of specific heat (section 7) and thermal expansivity (section 6). A better accuracy of the EOS is undoubtedly required than that of the Mie–Grüneisen EOS in order to describe experimental data, to reliably predict unmeasured properties, and in particular, to calculate the phase diagrams at high pressures (when a 10% error in P_{th} can substantially affect the estimated phase boundary slopes and positions).

9. Anderson–Grüneisen Parameters

Here, we consider the two useful Anderson–Grüneisen parameters in more detail [*Grüneisen*, 1926; *O. Anderson*, 1966a, 1967]: the isothermal δ_T parameter introduced above (see (31)) and the adiabatic δ_S parameter defined as

$$\delta_S \equiv -\frac{1}{\alpha K_S}\left(\frac{\partial K_S}{\partial T}\right)_P = \left(\frac{\partial \ln K_S}{\partial \ln \rho}\right)_P. \qquad (82)$$

Both parameters are used in geophysical and physical studies [*Chung*, 1973; *Barron*, 1979]. The parameter δ_T is largely applied in analyzing the $P - T$ behavior of α, K_T, and τ, and δ_S is used to estimate the temperature dependence of K_S and to treat the relations between elastic properties (elastic wave velocities) and thermodynamic data [*D. Anderson*, 1987; *O. Anderson et al.*, 1987; *Isaak et al.*, 1992; *Duffy and Ahrens*, 1992a, 1992b; *Agnon and Bukowinski*, 1990b].

As the temperature decreases in the range $T \lesssim 300$ K at $P = $ constant, both parameters δ_S and δ_T sharply increase due to decreasing α, but at high temperatures,

$T > \Theta$, they become more or less constant [*O. Anderson et al.*, 1992a]. From (16), we derive the identity relating δ_T and δ_S [*Birch*, 1952]

$$\delta_T = \delta_S + \gamma - \alpha\gamma T$$

$$\times \left[\delta_T - 1 - 2\hat{\alpha} + \frac{1}{\alpha C_P}\left(\frac{\partial C_P}{\partial T}\right)_P\right], \quad (83)$$

which was used to calculate the δ_T values listed in Table 3 and *Pankov et al.* [1997]. Deriving (83), we find in passing that

$$T\left(\frac{\partial\gamma}{\partial T}\right)_P$$

$$= \alpha\gamma T\left[\hat{\alpha} - \delta_T + 1 + \frac{1}{\alpha C_V}\left(\frac{\partial C_V}{\partial T}\right)_P\right]$$

$$= \alpha\gamma T(1 + \alpha\gamma T)\left[L + \hat{\alpha}\frac{\alpha\gamma T}{1 + \alpha\gamma T}\right. \quad (84)$$

$$\left. + \frac{\gamma}{1 + \alpha\gamma T} - \delta_T + 1\right],$$

where, for convenience, the notation

$$L \equiv \frac{C_P}{\alpha^2}\left(\frac{\partial\alpha/C_P}{\partial T}\right)_P, \quad (85)$$

is introduced.

The values of L and $(\partial\gamma/\partial T)_P$ at $P = 0$, calculated by (84) and (85), are also presented in Table 3 and *Pankov et al.* [1997].

Data for some minerals [*O. Anderson et al.*, 1992a] show that $(\partial\gamma/\partial T)_{P=0} \approx 0$ over a wide temperature range. Assuming that $(\partial\gamma/\partial T)_P = 0$ for $C_V = $ constant $(T > \Theta)$, (84) gives

$$\delta_T \approx \hat{\alpha} + 1. \quad (86)$$

Moreover, since $C_V = $ constant, this case results in $q = 0$, and consequently, according to (35) and (42),

$$\delta_T \approx K' - 1. \quad (87)$$

However, the estimation of δ_T by (42) for $q \sim 1$ is more accurate than the values from (87). Then, one might expect that in (84)

$$\left(\frac{\partial\gamma}{\partial \ln T}\right)_P / \alpha\gamma T \longrightarrow q,$$

for $C_V \longrightarrow$ constant.

Using (83), identity (84) can be rearranged to the form

$$\delta_T = \delta_S + \gamma - \frac{\alpha\gamma T}{1 + \alpha\gamma T}$$

$$\times \left[\gamma - \hat{\alpha} - \frac{1}{\alpha\gamma T}\left(\frac{\partial\gamma}{\partial \ln T}\right)_P\right]. \quad (88)$$

If the last term in (88) is small, then [*O. Anderson et al.*, 1992a]

$$\delta_T \approx \delta_S + \gamma. \quad (89)$$

This approximation is recommended for evaluating of the Anderson–Grüneisen parameters at high temperatures, when there are no sufficient data for applying (83) or (88).

In addition to the analysis of the parameter $\delta_T(P, T)$ described in sections 6 and 8, we consider the following features in the behavior of δ_T. 1) If $\gamma = \gamma(V)$, then $q = q(V)$, but generally speaking, $\delta_T = \delta_T(V, T)$ since $C_V = C_V(V, T)$ and $K' = K'(V, T)$. 2) If $C_V = C_V(T)$, then (42) holds true, and moreover, $\gamma = f(V)/C_V(T)$, $q = q(V)$, although, generally speaking, $K' = K'(V, T)$ and $\delta_T = \delta_T(V, T)$. Combining the former of these assumptions with the condition $K_T = K_T(V)$ (i.e., $\delta_T = K'$), we find

$$\left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T = 1 - q, \quad (90)$$

and C_V therefore takes the form

$$C_V(V, T) = \frac{A(V)}{B(T)}.$$

In section 6.2.2, the arguments were given for decreasing δ_T with pressure. The same behavior of this parameter follows from the approximation (42) since both K' and q decrease with pressure. The exact relations for the P and T derivatives of δ_T result from the definition of δ_T by (31)

$$\left(\frac{\partial\delta_T}{\partial P}\right)_T = -\frac{1}{\tau}\left[\delta_T\left(\frac{\partial\tau}{\partial P}\right)_T + \left(\frac{\partial K'}{\partial T}\right)_P\right], \quad (91)$$

$$\left(\frac{\partial\delta_T}{\partial T}\right)_P = -\frac{1}{\tau}\left[\delta_T\left(\frac{\partial\tau}{\partial T}\right)_P + \left(\frac{\partial^2 K_T}{\partial T^2}\right)_P\right]. \quad (92)$$

If the first term in (91) prevails, we have an unusual case $((\partial\delta_T)/(\partial P))_T > 0$. Neglecting the second temperature derivative in (92) (at least at room temperature), we find that $(\partial\delta_T/\partial T)_P < 0$. However, the approximation $\delta_T = K'$ (more realistic at $T > \Theta$) gives, by constast, $(\partial\delta_T/\partial T)_P > 0$ because of $(\partial K'/\partial T)_P > 0$. Experimental data indicate that $((\partial^2 K_T)/(\partial T^2))_P$ for $T > \Theta$ is negative and small in value [*O. Anderson et al.*, 1992a].

Finally, the EOS of type (28), which we used to calculate the thermal expansion coefficient by (36), allows us to determine the explicit pressure (or volume) dependence of K_T along an isotherm. Retaining in (36) only the terms involving dK_0'/dT, we obtain
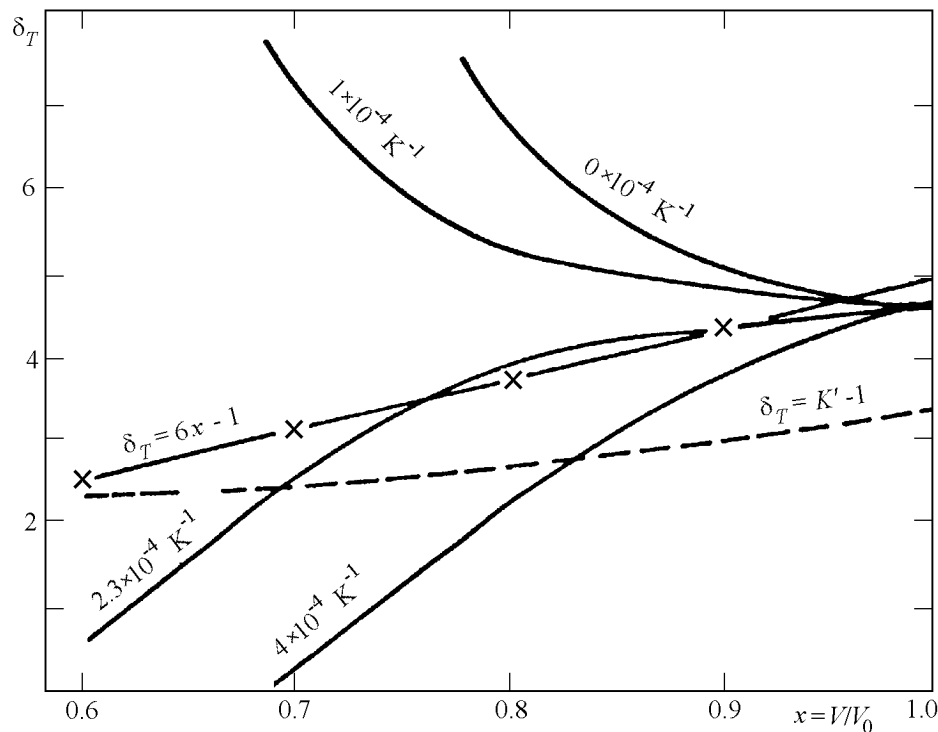
$$\frac{\delta_T}{\delta_{T0}} =$$

Figure 8. Parameter δ_T versus x at $T = $ constant. The solid lines are by (93), corresponding to the α curves in Figure 3. The crosses are by the power law corresponding to (48) [*O. Anderson et al.*, 1993] or $\delta_T = 6x - 1$ from (47) [*Chopelas and Boehler*, 1992]. The dashed line is the lower limit $\delta_T = K' - 1$ calculated by (28) and (37) (under the condition that $C_V = $ constant and $q \geq 0$).

$$= \frac{1 - K'\dfrac{P}{K_T} + \dfrac{K_0}{\alpha_0 \delta_{T0} K_T}\dfrac{dK'_0}{dT}\left(\dfrac{\partial f}{\partial K'_0} + x\dfrac{\partial f'}{\partial K'_0}\right)}{1 - \dfrac{P}{K_T}\delta_{T0} + \dfrac{K_0}{\alpha_0 K_T}\dfrac{\partial f}{\partial K'_0}\dfrac{dK'_0}{dT}},$$

$$\tag{93}$$

where f' denote the derivative of f with respect to x. This approximation generalizes the similar Birch formula that follows from (93) for $dK'_0/dT = 0$ [*Birch*, 1968]. However, when using usual EOS types, δ_T from the Birch formula increases with P (except for the Murnaghan EOS for which the behavior of δ_T depends on the sign of the difference $K' - \delta_{T0}$). Again, we convince ourselves that the term with derivative dK'_0/dT is important in analyzing the thermal expansion by (28).

Figure 8 shows several curves of $\delta_T(x)$ calculated using (93) and EOS (37), which correspond to the curves of α in Figures 1 and 3 (the straight line $\delta_T = 6x - 1$ by (47) is also drawn for comparison). The favored value of dK'_0/dT is $2 \cdot 10^{-3}$ K^{-1} (see section 6.2), and deviations from it substantially affect the δ_T values at compressions in the lower mantle. At high temperatures, according to (42), we have also the lower limit for δ_T, $\delta_T > K' - 1$ [*O. Anderson et al.*, 1992a].

10. Bulk Moduli

10.1. *P–V–T* derivatives

Elastic moduli and their $P - V - T$ derivatives are the characteristics constituting the basis of the Earth's interior thermodynamics [*Birch*, 1952, 1961; *Sumino and O. Anderson*, 1984; *D. Anderson*, 1967, 1987, 1989; *O. Anderson et al.*, 1992a; *Duffy and D. Anderson*, 1989; *Bina and Helffrich*, 1992; *Duffy and Ahrens*, 1992a, 1992b]. These quantities also serve as parameters of EOS's. The simplest estimates of adiabatic and isothermal bulk moduli at high pressure are given by their linear pressure dependences, which, however, begin to overestimate the bulk modulus at a compression of about $x < 0.85$. The $P - T$ variation of the pressure derivative was considered in many papers devoted to EOS's (see section 3). In order to assess the applicability of empirical EOS's, one often uses a relation between the first $K' \equiv (\partial K_T/\partial R)_T$ and second $K'' \equiv (\partial^2 K_T/\partial P^2)_T$ pressure derivatives at $P = 0$ [*Pankov and Ullmann*, 1979a; *Jeanloz*, 1989; *O. Anderson*, 1986; *Hofmeister*, 1991b]. Values of K' and

KK'' at $P = 0$ generally lie in the intervals 4–6 and $-(5-10)$, respectively. The uncertainty in $(\partial K_S/\partial P)_T$ (measured by ultrasonic or Brillouin scattering methods) can reach 1–5% (with allowance for data from various laboratories) or, in some cases, 20% and even 50%. Anomalous values of K' and K'' are sometimes reported (see references in tables of *Pankov et al.* [1997]): for example, $K' = 5 - 7$ (garnet), $K' = 9 - 14$ (pyroxene), and $KK'' = -60$ (spinel), which are assumed to take on more usual values as pressure increases.

Let us turn our attention to the relations between the adiabatic–isothermal derivatives of K_S and K_T. Changing the variables P and S to P and T, we find

$$\left(\frac{\partial K_S}{\partial P}\right)_S = \left(\frac{\partial K_S}{\partial P}\right)_T - \delta_S \alpha \gamma T, \qquad (94)$$

where δ_S is defined by (82). The derivative $(\partial K_S/\partial P)_S$ characterizes the curvature of an adiabatic $P - V$ or a Hugoniot curve. Further, from (16)

$$\left(\frac{\partial K_S}{\partial P}\right)_T = K'(1 + \alpha \gamma T)$$

$$+ K_T T \left[\alpha \left(\frac{\partial \gamma}{\partial P}\right)_T + \gamma \left(\frac{\partial \alpha}{\partial P}\right)_T\right]. \qquad (95)$$

Eliminating $(\partial \gamma/\partial P)_T$ with the help of (8) and (17) (or (122)) and using (58), we find

$$\left(\frac{\partial K_S}{\partial P}\right)_T = K' + \alpha \gamma T \left(2K' - 2\delta_T - 1\right)$$

$$+ (\alpha \gamma T)^2 \left(K' - 2\delta_T + \hat{\alpha}\right). \qquad (96)$$

Substituting (94) for $(\partial K_S/\partial P)_T$ and (93) for δ_S, we arrive at the *Birch* [1952] formula

$$\left(\frac{\partial K_S}{\partial P}\right)_T = K' + \alpha \gamma T (2K' - 3\delta_T - 1 + \gamma)$$

$$+ (\alpha \gamma T)^2 \left(K' - 3\delta_T + 3\hat{\alpha} + 1 - \frac{1}{\alpha C_P}\left(\frac{\partial C_P}{\partial T}\right)_P\right). \qquad (97)$$

The difference between the adiabatic–isothermal derivatives of K_S and K_T at normal conditions are generally small (1–2% for mantle minerals). Data and estimations by (94)–(97) show that we usually have

$$\left(\frac{\partial K_S}{\partial P}\right)_S < \left(\frac{\partial K_S}{\partial P}\right)_T < K'$$

(except for FeO for which $(\partial K_S/\partial P)_T$ is poorly known [*Pankov et al.*, 1997]); however, *D. Anderson* [1989] indicated the inverse inequality

$$\left(\frac{\partial K_S}{\partial P}\right)_T > K' K_S/K_T.$$

For our high-temperature estimates given in Table 3 and *Pankov et al.* [1997], it was arbitrarily assumed that

$$\left(\frac{\partial K_S}{\partial P}\right)_T = \text{const} \quad \left(\text{or } \partial^2 K_S/\partial P \partial T \lesssim 10^{-5} \text{K}^{-1}\right).$$

Hence, using (94)–(97), we found substantial differences (up to 10–30%) between the pressure derivatives of K_S and K_T at high temperatures. In fact, the differences are of the same order of magnitude as the derivative increments due to increasing temperature. Specifically, the estimated $\partial^2 K_T/\partial P \partial T$ values are $3.5 \cdot 10^{-4}$ (stishovite), $2 \cdot 10^{-4}$ (ilmenite), $3 \cdot 10^{-4}$ (Mg-perovskite), and $1.7 \cdot 10^{-4}$ (MgO) and do not exceed $1 \cdot 10^{-4}$ for other minerals (although some estimates appear to be negative).

Isaak [1993] estimated $\partial^2 K_T/\partial P \partial T$ using an identity of type (91) and Boehler's data on the adiabatic temperature gradient (see also section 12.2). He found $\partial^2 K_T/\partial P \partial T = (3.9 \pm 1.0) \cdot 10^{-4}$ and $(3.3 \pm 0.9) \cdot 10^{-4}$ K^{-1} for MgO and olivine, respectively. Furthermore, he showed this derivative to decrease 30% as the pressure increases isothermally to 100 GPa. A similar order of magnitude was found from shock wave data to be a lower limit for this derivative value [*Duffy and Ahrens*, 1992a] (see also sections 6 and 9).

In addition to the analysis of the mixed derivatives, we give the following identity

$$\frac{1}{\alpha \delta_S} \left(\frac{\partial}{\partial T}\left(\frac{\partial K_S}{\partial P}\right)_S\right)_P$$

$$= -\left(\frac{\partial K_S}{\partial P}\right)_S - \left(\frac{\partial \ln \delta_S}{\partial \ln \rho}\right)_S + \delta_S \left(1 + \alpha \gamma T\right), \qquad (98)$$

which we derived from (94), using (127) and $(\partial \gamma/\partial T)_P$ from (88). Note that a similar relation of *Bukowinski and Wolf* [1990] is different from (98) (because of either a reprint or mistake). To give an example, we substitute in (98) the values typical of the lower mantle: $(\partial K_S/\partial P)_S = 4$, $\alpha \gamma T = 0.1$, $((\partial \ln \delta_S)/(\partial \ln \rho))_S = -1$, and $\delta_S = 3$ for $x = 1$ and $\delta_S \lesssim 2$ for $x = 0.7$. Then,

$$\left(\frac{\partial(\partial K_S/\partial P)_S}{\partial T}\right)_P \gtrsim 0.8 \cdot 10^{-4},$$

which is in agreement with the preceding estimates.

When considering the temperature behavior of K_S and K_T, the Anderson–Grüneisen parameters δ_S and δ_T are represented in the form of (29) [*D. Anderson*, 1987; *Duffy and D. Anderson*, 1989; *O. Anderson et al.*, 1992a], which can be rewritten as

$$\delta_S = -\frac{1}{\alpha K_S}\left(\frac{\partial K_S}{\partial T}\right)_V + \left(\frac{\partial K_S}{\partial P}\right)_T \frac{K_T}{K_S}$$

$$= \left(\frac{\partial \ln K_S}{\partial \ln \rho} \right)_P = -\delta_V^S + \left(\frac{\partial K_S}{\partial P} \right)_T \frac{K_S}{K_T} \quad (99)$$

$$\approx -\delta_V^S + K',$$

$$\delta_T = \left(\frac{\partial \ln K_T}{\partial \ln \rho} \right)_P$$

$$= -\frac{1}{\alpha K_T} \left(\frac{\partial K_T}{\partial T} \right)_V + K' = -\delta_V^T + K'. \quad (100)$$

In section 9, we considered the principal regularites in the variation of δ_S and δ_T with pressure and temperature (some decrease of them with T in the vicinity of $T = 300$ K, the trend to constant values at $T > \Theta$, and the decrease with pressure). Now we dwell on the contributions of the intrinsic δ_V^S and δ_V^T and extrinsic K' anharmonic terms in (99) and (100).

D. Anderson [1988, 1989] pointed out that the temperature variation of the bulk modulus at $P = $ constant mostly occurs by the variation in α; i.e., here, the extrinsic anharmonicity generally prevails and enhances with temperature (due to increasing K'). The estimates given in Table 3 and *Pankov et al.* [1997] show that, at $T = 300$ K, we have $\delta_V^T < 0$ (except very uncertain data for FeO); most of the estimates falls into an interval between -1 and -2 (although it was found $\delta_V^T = -17$, -5, and -3.9 for coesite, stishovite, and fictive Fe-perovskite phase, respectively). According to *D. Anderson* [1989], the values of δ_V^T are typically between -4 and -1 (his table 5, however, contains values outside this interval: 2.2 for orthopyroxene, -5.3 for SrTiO$_3$, and -19 for CaCO$_3$). The parameter δ_V^S satisfies the inequality $|\delta_V^S| > 2$ for 11 out of 54 minerals considered by D. Anderson (specifically, $\delta_V^S = -4.1$ (GeO$_2$), 3.8 (orthopyroxene), -3.1 (SrTiO$_3$), and -18 (CaCO$_3$). At high temperatures, δ_V^T can be either positive or negative (between -1 and 1), and $|\delta_V^S|$ is generally positive, lying in the interval 0–1.5 [*Pankov et al.*, 1997]. Thus, as temperature increases, $|\delta_V^T|$, on average, decreases, but $|\delta_V^S|$ increases. The contribution of δ_V^S/δ_S to (99) is usually less than 10–30% at 300 K and does not exceed 15–60% at high temperatures. Accordingly, δ_V^T contributes no more than 30–40% in (100) at 300 K and usually less than 10% at high temperatures. From this analysis, it follows that the extrinsic anharmonic term, although it generally dominates in the derivatives of K_S and K_T, decreases its contribution in the case of K_S and increases its contribution in the case of K_T. The decrease of δ_V^T with temperature leads to the approximation

$$\delta_V^T \approx 0, \qquad \delta_T \approx K', \qquad K_T \approx K_T(V) \quad (101)$$

and additionally, in view of (89) and (99),

$$\delta_V^S \approx \delta_V^T + \gamma \approx \gamma. \quad (102)$$

Thus, at high temperatures, namely the isothermal, rather than adiabatic bulk modulus becomes depending mostly on volume (i.e., temperature-independent function).

10.2. Interpretation of seismic tomography data

In his analysis of the thermodynamic properties of the lower mantle, *D. Anderson* [1987, 1988, 1989] relies on seismic tomography and geoid data and assumes that the observed horizontal velocity anomalies are caused by temperature variations. *Stacey* [1992] showed, however, that it is not possible to explain the anomalies with a purely temperature effect, since in such a case, the geoid highs would be too great. Other hypotheses proposed to interpret the seismic anomalies were related to inhomogeneities of composiion, or partial melting, or even the presence of small amounts of fluids [*Price et al.*, 1989; *Duffy and Ahrens*, 1992b; and others]. Nevertheless, following D. Anderson, below, we estimate the thermodynamic parameters for the lower mantle, considering the temperature effect formally as a limiting case.

Based on the PREM model, the formula for the acoustic Grüneisen parameter, and tomography data, we have in the lower mantle $(\partial K_S / \partial P)_S = 3 - 3.8$, $\gamma = 1.2 \pm 0.1$, and $\delta_S = 1 - 1.8$. Consequently, using (89), (94), (96), (99), and (100), we find $\delta_T \approx \delta_S + \gamma = 2.2 - 3.0$, $K' = 3 - 3.8$ (a small correction can be introduced with the help of $\alpha = \alpha_0 x^{\delta_T}$ for $\alpha_0 = 4 \cdot 10^{-5}$ K^{-1} and $T \approx 2000$–3000 K), $\delta_V^S \approx K' - \delta_S = 1.2 - 2.8$, and $\delta_V^T = \delta_V^S - \gamma = -0.1 - 1.7$. If a greater uncertainty is assumed for γ, say ± 0.4, then $\delta_T \sim 1.9 - 3.3$ and $\delta_V^S \sim -0.4 - 2.0$. Thus, although the extrinsic anharmonic effects weaken with pressure, they still prevail under the lower mantle conditions ($K' > \delta_V^S$ or $|\delta_V^T|$). The intrinsic anharmonic term δ_V^S significantly increases with pressure, but its isothermal analog δ_V^T can either increase or decrease and reach zero. D. Anderson, by reference to experimental data, points out the case of $\delta_V^T \approx 0$, which yields $\delta_V^S \sim \gamma = 1.2$.

However, this value of δ_V^S disagrees with data for such a representative lower-mantle material as periclase. Using $\delta_V^T = 0$ and $\delta_T = K' \approx 3.2 - 3.5$ for $x = 0.7$ and the Birch–Murnaghan EOS for MgO, we find $\delta_S \sim \delta_T - \gamma = 2.2 - 2.5$ for $\gamma = \gamma_0 x$ ($q = 1$, see (119)). These values of δ_T and δ_S are, on average, still exceed the results inferred from seismic models. *O. Anderson et al.* [1992b] noted that data for MgO can be reconciled with seismic results by assuming that $q < 1$. In particular, our analysis leads to the following consistent sequence of values: $\delta_V^T \gtrsim 0.2$, $q \lesssim 0.8$, $\gamma = \gamma_0 x^q \gtrsim 1.1$

(for $x = 0.7$), $\delta_T = K' - \delta_V^T \lesssim 3 - 3.3$, and $\delta_S \lesssim 1.9 - 2.2$. In any case, the consistency to seismic data could be found in this manner if the values derived from seismic tomography were explained by only horizontal variations of temperature.

10.3. Estimation of K_S at high temperature

10.3.1. The consideration of the temperature behavior of K_S at $P = 0$ will be added by the following two methods. One of them uses the condition $\delta_S = \delta_S^* =$ constant [*O. Anderson*, 1988; *Duffy and D. Anderson*, 1989], and in view of (99), yields the power law

$$K_S = K_S^* (\rho/\rho^*)^{\delta_S}, \tag{103}$$

which we used to estimate the values listed in Table 2 and *Pankov et al.* [1997].

Another approach proposed by *O. Anderson* [1989] and extended by *O. Anderson et al.* [1992a] is based on data for enthalpy. We obtain the relation of K_S to enthalpy using a somewhat different procedure, namely, the formula $\gamma = \alpha K_S V / C_P$ from which the derivative $(\partial K_S / \partial H)_P$ is found, and thus, approximately,

$$K_S = K_S^* - \delta_S^* \gamma^* \rho^* (H - H^*), \tag{104}$$

where the asterisk marks the values at a fixed temperature. By using the parameter values from Table 2 and *Pankov et al.* [1997], as well as data for enthalpy, we estimated K_S by (104) for a number of minerals (Table 4). One can see that the O. Anderson's method is quite efficient: the uncertainty of the estimated values at high temperatures is 2–5%. It is also clear that both methods described above would give more accurate results when high-temperature values for K_S^*, ρ^*, γ^*, H^*, and δ_S^* are used in the respective formulas.

10.3.2. In conclusion to this analysis, we show the dependence of K_S versus T at $P = 0$ (Figure 9) calculated by the Mie–Grüneisen EOS with $\gamma = \gamma_0 x^q$ for three minerals considered in sections 6–8. Comparing the K_S curves for various values of $q = 0 - 2$ with experimental data, we see that it is possible to choose appropriate values of q consistent to the data. However, considering the results presented for the same EOS's in sections 6–8, it is not always possible to find such values of q for which the EOS becomes consistent to data simultaneously for α, C_P, τ, and K_S. Thus, as in sections 6–8, we conclude that the thermal part of the Mie–Grüneisen EOS does not provide suffuciently high accuracy of all the thermodynamic parameters calculated from this EOS.

11. Thermodynamic Grüneisen Parameter

The thermodynamic Grüneisen parameter is defined by (8) or (14), which further lead to several useful identities

$$\gamma = V \left(\frac{\partial P}{\partial E} \right)_V = V \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial E} \right)_V$$

$$= \frac{V (\partial S / \partial V)_T}{V (\partial S / \partial T)_V} = \frac{V \partial^2 F / \partial V \partial T}{T (\partial^2 F / \partial T^2)_V} = - \left(\frac{\partial \ln T}{\partial \ln V} \right)_S \tag{105}$$

The typical values of γ by (8) or (14) range from 1 to 2 (see, e.g., Table 2 and *Pankov et al.* [1997]). Of 54 minerals treated by *D. Anderson* [1989], only five have γ greater than 2, and none has γ over 3. Low values of γ are seldom encountered: e.g., $\gamma = 0.4$ for α-quartz, 0.3 for coesite, and even $\gamma < 0$ for U_2O, AgJ, and β-quartz.

11.1. P–V–T derivatives of γ

The logarithmic derivatives of γ with respect to V (or P) are characterized by the parameter q, for which from (8) and (100), we find

$$q = \left(\frac{\partial \ln \gamma}{\partial \ln V} \right)_T = -K_T \left(\frac{\partial \ln \gamma}{\partial \ln P} \right)_T$$

$$= 1 - \frac{V}{\gamma C_V} \left(\frac{\partial K_T}{\partial T} \right)_V - \left(\frac{\partial \ln C_V}{\partial \ln V} \right)_T \tag{106}$$

$$= 1 + \delta_T - K' - \left(\frac{\partial \ln C_V}{\partial \ln V} \right)_T$$

$$= 1 - \delta_V^T - \left(\frac{\partial \ln C_V}{\partial \ln V} \right)_T \tag{107}$$

$$= 1 + \delta_T - K' - \alpha \gamma T (\hat{\alpha} + K' - 2\delta_T). \tag{108}$$

As noted earlier (see (57) or (69) and (8)), in general, the $C_V =$ constant case leads to $\gamma = \gamma(V)$, and therefore, $q = q(V)$ or $q =$ constant. If C_V is only temperature-dependent, there are three possibilities: (1) $q = q(V)$, (2) $q =$ constant $\neq 1$ (i.e., $\delta_V^T =$ constant $\neq 0$), and (3) $q = 1$ ($\delta_V^T = 0$, $K' = \delta_T(V)$, and $\tau = \alpha K_T =$ constant). Thus, both $C_V =$ constant and $C_V = C_V(T)$ conditions result in the case that the two inequalities are equivalent:

$$0 \leq q \leq 1 \quad \text{and} \quad 0 \leq \delta_V^T = K' - \delta_T \leq 1 \tag{109}$$

If we simply assume that γ is only volume-dependent, then from (14), (33), and (106),

Table 4. Estimated and measured values of K_S at normal pressure and high temperatures[*]

Minerals	Temperature, K	K_S (GPa) for $\delta_s(300K) = \delta_S = $ const		K_S (GPa) by the method of O. Anderson $\Delta K_S \sim H$		K_S (GPa) from measurements [O. Anderson et al., 1992a]
MgO, periclase	1800	135.7	(2.3)	134.8	(1.5)	132.7
Al$_2$O$_3$, corundum	1800	218.3	(1.4)	217.1	(2.1)	221.8
SiO$_2$, α-quartz	1000	30.4	(5.5)	28.8		—
SiO$_2$, coesite	1000	82.8	(2.1)	81.1		—
SiO$_2$, stishovite	1800	222.4	(0.8)	220.6		—
CaO, lime	1200	97.4	(1.3)	97.6	(1.1)	98.7
FeO, wüstite	900	156.8	(0.4)	157.5		—
Mg$_2$SiO$_4$, forsterite	1700	101.5	(2.2)	101.6	(2.6)[**]	103.8
Mg$_2$SiO$_4$, β-spinel	1700	139.5	(2.3)	136.4		—
Mg$_2$SiO$_4$, γ-spinel	1700	152.6	(3.5)	147.4		—
MgSiO$_3$, enstatite	1700	89.6	(4.4)	85.8		—
MgSiO$_3$, ilmenite	1700	179	(3.8)	186		—
MgSiO$_3$, perovskite	1700	172	(4.9)	180.8		—
MgSiO$_3$, garnet	1700	121	(8.0)	112		—
Fe$_2$SiO$_4$, fayalite	1500	105.7	(4.3)	101.3		—
Fe$_2$SiO$_4$, β-spinel	1700	137	(1.0)	138.4		—
Fe$_2$SiO$_4$, γ-spinel	1700	170	(2.4)	166.0		—
FeSiO$_3$, ferrosilite	1700	78.5	(2.6)	76.6		—
FeSiO$_3$, perovskite	1700	207	(7.6)	192.4		—
Grossular	1300	148	(3.0)	—		152.6
Pyrope	1200	149.8	(2.2)	—		153.2
Olivine, Fo 90	1500	103.3	(4.2)	—		107.8
Olivine, Fo 92	1400	108.6	(3.8)	—		112.9

[*] Given in parentheses are the deviations (in percentages) from the measured K_S; when the latter is not available, the difference (in percentages) between two indicated values of K_S is given.
[**] Extrapolation from $T = 400$ K, using the O. Anderson et al. [1992a] data. The extrapolation from $T = 300$ K gives $K_S = 97.4$ GPa (6.2% deviation).

$$\left(\frac{\partial K_S}{\partial T}\right)_V = \left(\frac{\partial K_T}{\partial T}\right)_V (1 + \alpha\gamma T) + K_T$$

$$\times \left[\left(\frac{\partial \alpha}{\partial T}\right)_V \gamma T + \alpha\gamma\right]. \qquad (110)$$

Placing in (110) for $(K_S/\partial T)_V$ by identity (99),

$$q = 1 + \gamma - \left(\frac{\partial K_S}{\partial P}\right)_T + (1 + \alpha\gamma T)\delta_S \qquad (111)$$

However, in the general case, $\gamma = \gamma(V, T)$, and from the formula for γ in (18), we find

$$\frac{K_S}{\gamma}\left(\frac{\partial \gamma}{\partial P}\right)_T$$

$$= \left(\frac{\partial K_S}{\partial P}\right)_T - 1 - \delta_S - \gamma - \alpha\gamma T(L + 1), \qquad (112)$$

which, upon excluding L by (85), yields the important identity [Bassett et al., 1968]

$$q = \delta_S(1 + \alpha\gamma T) + 1 - \left(\frac{\partial K_S}{\partial P}\right)_T$$

$$+ \gamma\left[1 + \left(\frac{\partial \ln \gamma}{\partial \ln T}\right)_V\right] \qquad (113)$$

$$= \delta_S + 1 - \left(\frac{\partial K_S}{\partial P}\right)_S + \gamma\left[1 + \left(\frac{\partial \ln \gamma}{\partial \ln T}\right)_V\right],$$

For $\gamma = \gamma(V)$, this identity is reduced to (111).

In section 6, we have already referred to some data on values of q. In general, values of q can be inferred
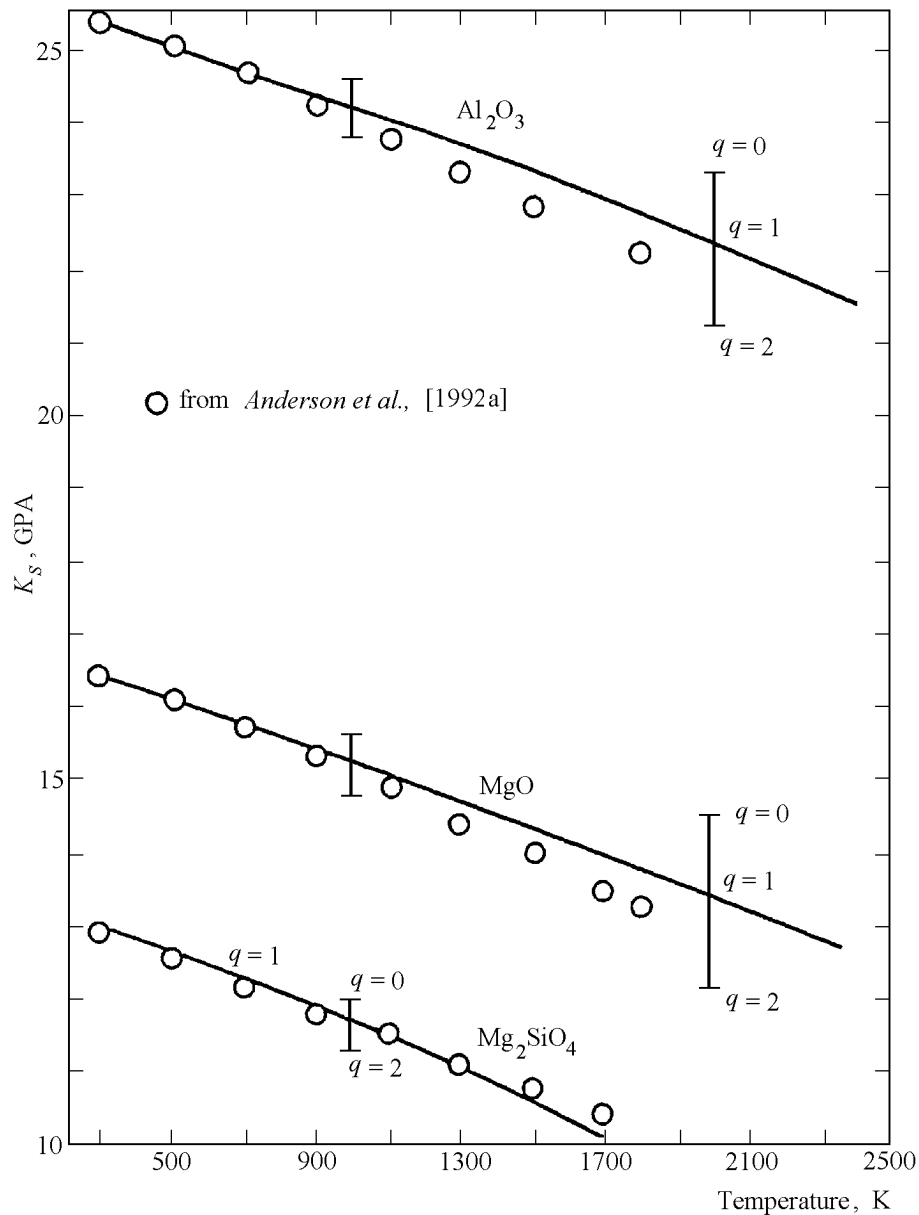
Figure 9. Adiabatic bulk modulus versus temperature at $P = 0$ for three minerals. The solid lines are from the Mie–Grüneisen EOS (as in Figures 4–7). The cicles are data of *O. Anderson et al.* [1992a].

from the following sources: 1) thermodynamic estimation by (108) or (111), 2) fit of the Mie–Grüneisen type EOS to data on $\alpha(T)$, $C_P(T)$, and $K_S(T)$ at $P = 0$, 3) shock wave data [e.g., *McQueen,* 1991; *Duffy and Ahrens,* 1992a], 4) adiabatic temperature gradient measurements [*Boehler,* 1982, 1983], 5) spectroscopy of solids [e.g., *Reynard et al.,* 1992; *Williams et al.,* 1987], 6) theoretical EOS models [e.g., *Isaak et al.,* 1990], 7) analysis of geophysical data [*O. Anderson,* 1979b; *D. Anderson,* 1989]. The values of q estimated by (108) and given in Table 3 and *Pankov et al.* [1997], fall into

the interval 0.5–2, except for the high values for coesite (about 17), fayalite (2–3), and Fe-perovskite (4–5). Small negative values were also found for enstatite and FeO (probably, due to inaccurate input data). With increasing T at $P = $ constant or with increasing P at T (or $S = $ constant), q decreases (see also section 6).

For the temperature derivative of γ, we again have the expansion of type (29)

$$\frac{1}{\alpha\gamma}\left(\frac{\partial\gamma}{\partial T}\right)_P = q + \frac{1}{\alpha}\left(\frac{\partial\ln\gamma}{\partial T}\right)_V, \qquad (114)$$

where the intrinsic anharmonicity term can be evaluated using (18) and (85)

$$\frac{1+\alpha\gamma T}{\alpha\gamma T}\left(\frac{\partial\gamma}{\partial\ln T}\right)_V$$

$$= L - 2\delta_S - \gamma + \left(\frac{\partial K_S}{\partial P}\right)_T - \alpha\gamma T\delta_S. \qquad (115)$$

This term is usually negative and completely prevails in (114) at $T < \Theta$, but at high temperatures, its value is comparable to q. Thus, the frequently used assumption that $\gamma = \gamma(V)$ is unsatisfactory in the general case, and the temperature effect on the Grüneisen parameter can serve as a measure of the validity of the Mie–Grüneisen EOS [*Molodets*, 1998].

Another suitable representation of $(\partial\gamma/\partial T)_V$ follows from (8) and (69) [*Stacey*, 1977b]

$$T\left(\frac{\partial\gamma}{\partial T}\right)_V$$

$$= T\left[\left(\frac{\partial\tau}{\partial T}\right)_V\frac{V}{C_V} - \frac{\gamma}{C_V}\left(\frac{\partial C_V}{\partial T}\right)_V\right] \qquad (116)$$

$$= \left(\frac{\partial\ln C_V}{\partial\ln V}\right)_T - \gamma\left(\frac{\partial\ln C_V}{\partial\ln T}\right)_V = \left(\frac{\partial\ln C_V}{\partial\ln V}\right)_S.$$

If $\gamma = \gamma(V)$, then either $C_V = C_V(S)$ or $C_V =$ constant. The case $C_V(S)$ results in

$$\gamma = \frac{(\partial\ln C_V/\partial\ln V)_T}{(\partial\ln C_V/\partial\ln T)_V}. \qquad (117)$$

Moreover, (117) leads to $C_V(V,T) = C_V(\Theta/T)$ and $\Theta/T = f(S)$, so that γ is represented as $\gamma = -d\ln\Theta/d\ln V$, where Θ is a characteristic temperature.

11.2. Some explicit volume dependences of γ

The frequently used volume dependences of the latice Grüneisen parameter were given in section 6. The *Rice* [1965] formula is also of interest

$$\gamma = \frac{\gamma_0 x}{1 - \gamma_0(x-1)}, \qquad (118)$$

which is derived from (110) under the condition that

$$\left(\frac{\partial K_S}{\partial T}\right)_V = 0 \quad \text{and} \quad \gamma = \gamma(V).$$

The inequality $(\partial K_S/\partial T)_V > 0$ (see section 10 and *D. Anderson* [1989]) holds true of many materials and therefore gives a lower limit for their dependence $\gamma(V)$, i.e., $q \le 1 + \gamma$ and $\gamma \ge \gamma(x)$ by (118). This limit was previously found from the Mie–Grüneisen EOS [*Kalinin*

and Panov, 1972], but it also follows from the given thermodynamic consideration.

Equation (118) can be considered a partial case of the more general representation $\gamma = \gamma(V, S)$. We introduce a parameter λ defined as

$$\lambda \equiv \frac{1}{\gamma T}\left(\frac{\partial\Phi}{\partial S}\right)_V = \delta_V^S(1 + \alpha\gamma T)$$

$$= 1 + \gamma - \left(\frac{\partial\ln\gamma}{\partial\ln V}\right)_S = 1 - \left(\frac{\partial\ln\gamma T}{\partial\ln V}\right)_S, \qquad (119)$$

where $\Phi = K_S/\rho$. Assuming that $\lambda = \lambda(S)$ or $\lambda =$ constant and using (119) and (105), we find by integration that

$$\gamma = \frac{\gamma_0 x^{1-\lambda}}{1 - \frac{\gamma_0}{1-\lambda}(x^{1-\lambda} - 1)} \text{ for } \lambda \ne 1,$$

$$\gamma = \frac{\gamma_0}{1 - \gamma_0\ln x} \text{ for } \lambda = 1 \qquad (120)$$

$$\gamma = \frac{\gamma_0 x}{1 - \gamma_0(x-1)} \text{ for } \lambda = 0,$$

where $\gamma_0 = \gamma_0(S)$ and $V_0 = V_0(S)$. These dependences of $\gamma(x)$ for various λ are illustrated in Figure 10. One can see that they are quite sensitive to variations of λ in the interval from 0 to 1.

12. Adiabatic Temperature Gradient

In geophysics, the conditions close to adiabatic are realized in the convecting mantle and core, as well as in seismic wave propagation. Furthermore, the state at the initial part of Hugoniot are close to adiabatic. Adiabats of a given material form a one-parametric family of curves. In this case, the temperature and pressure are related by the adiabatic gradient τ_S, which, considering its definition by (10) and relations in section 2, can be written in the form

$$\tau_S = \frac{\gamma T}{K_T(1 + \alpha\gamma T)} = \frac{\alpha\gamma T}{\tau(1 + \alpha\gamma T)}$$

$$= \frac{1}{\tau}\left(1 - \frac{C_V}{C_P}\right). \qquad (121)$$

Typical values of τ_S found by (121) are given in Table 2 and *Pankov et al.* [1997].

Direct measurements of τ_S at high pressures and temperatures were made in a series of works [*Dzhavadov*, 1986; *Boehler and Ranakrishnan*, 1980; *Boehler*, 1982, 1983]. *Chopelas and Boehler* [1992] reported corrections to the *Boehler* [1982] initial results on τ_S.
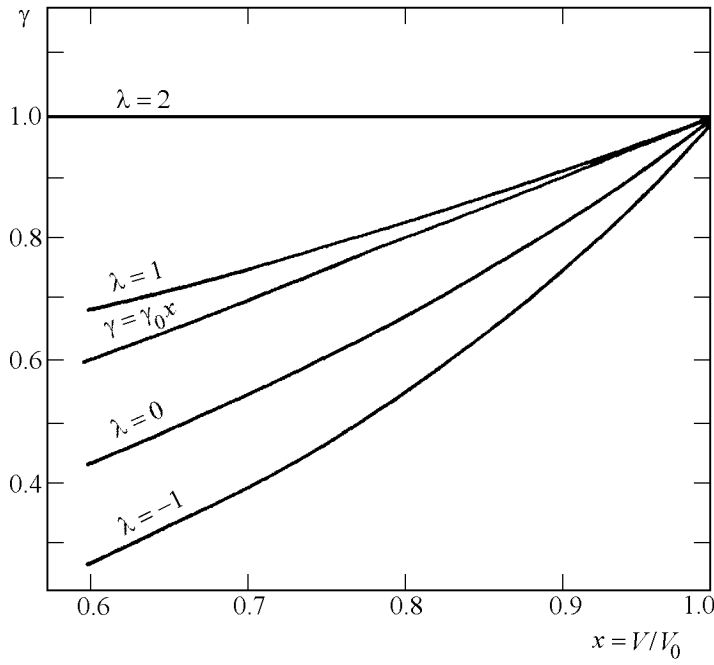
Figure 10. The Grüneisen parameter versus volume calculated by (120) for $\gamma_0 = 1$.

12.1. P–V–T derivatives of τ_S

We consider the basic identities and approximaions for the derivatives. Denoting by n the logarithmic volume derivative of τ_S and using q by (106), we have

$$n \equiv \left(\frac{\partial \ln \tau_S}{\partial \ln V}\right)_T = -K_T \left(\frac{\partial \ln \tau_S}{\partial P}\right)_T$$

$$= q + \frac{K_T}{K_S} \left(\frac{\partial K_S}{\partial P}\right)_T = 1 + \delta_T + K_T \left(\frac{\partial \ln C_P}{\partial P}\right)_T \quad (122)$$

(compare with (45)).

Formula (122) can be represented in various forms, using q by (113), (115), and (58). It is clear that n decreases by isothermal or adiabatic compression. The simplest estimate of n is given by assuming that

$$K_S \approx K_T \quad \text{and} \quad \left(\frac{\partial K_S}{\partial P}\right)_T \approx K',$$

hence,

$$n \approx q + K'. \quad (123)$$

The typical values of $q = 1$–2 and $K' = 4$–5 yield $n \cong 5 - 7$. If we neglect the last term in (122) at $T > \Theta$, then $n \cong 1 + \delta_T$ [*Chopelas and Boehler*, 1992].

Changing from variables (V, S) to (V, T), the adiabatic derivative with respect to volume takes the form

$$n_S \equiv \left(\frac{\partial \ln \tau_S}{\partial \ln V}\right)_S = 1 + \delta_S$$

$$= n - \gamma T \left(\frac{\partial \ln \tau_S}{\partial T}\right)_V \quad (124)$$

$$= n(1 + \alpha \gamma T) - \gamma \left(\frac{\partial \ln \tau_S}{\partial \ln T}\right)_P.$$

Approximation (89) and $n \cong 1 + \delta_T$ give $n_S \cong n - \gamma$. Writing the derivative of τ_S with respect to T in the form of (29),

$$\left(\frac{\partial \ln \tau_S}{\partial \ln V}\right)_P = \frac{1}{\alpha} \left(\frac{\partial \ln \tau_S}{\partial T}\right)_V + n \quad (125)$$

or after substituting $(\partial \ln \tau_S/\partial T)_V$ by (124),

$$\left(\frac{\partial \ln \tau_S}{\partial \ln T}\right)_P = \frac{1}{\gamma}\left[n(1 + \alpha \gamma T) - 1 - \delta_S\right]. \quad (126)$$

The values of $((\partial \ln \tau_S)(\partial \ln V))_P$ and n (an extrinsic anharmonic contribution) calculated by (126) and (122) are given in Table 2 and *Pankov et al.* [1997]. They show that the intrinsic anharmonic term dominates in (125).

Note that the τ_S parameter occurs in any expression when changing variables P, S to P, T: for example,

$$\left(\frac{\partial \delta_T}{\partial P}\right)_S = \left(\frac{\partial \delta_T}{\partial P}\right)_T + \left(\frac{\partial \delta_T}{\partial T}\right)_P \tau_S \quad (127)$$

which was used in deriving (98).

12.2. Explicit volume dependences of τ_S

For a moderate compression, the volume dependence of τ_S can be described by the power law

$$\tau_S = \tau_{S0} x^n, \tag{128}$$

where $n = n(T)$ or constant, $\tau_{S0} = \tau_{S0}(T)$ and $V_0 = V_0(T)$. This formula was used to fit the measured τ_S values to $P = 50$ kbar and $T = 1000$ K [*Boehler and Ramacrishnan*, 1980; *Boehler*, 1982].

However, *Chopelas and Boehler* [1992], accounting for the variation of δ_T with V (see (46) and (47)), found that the linear dependence of $\ln \tau_S$ on V ($n = mx$) better describes teir data on τ_S than the power law, and consequently,

$$\tau_S = \tau_{S0} e^{mV_0(x-1)}, \tag{129}$$

where constant m is determined by the approximation

$$m \approx \frac{1}{x}\left(1 + \delta_T - \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T\right) \tag{130}$$

(see (122), where C_P is approximately C_V). Thus, on the condition that $(\partial \ln C_V / \partial \ln V)_T$ is independent of V, the derivative $(\partial \delta_T / \partial x)_T$ can be found given knowledge of the m value. *Isaak* [1993] applied this method to evaluate the derivative $\partial^2 K_S / \partial P \partial T$ with the help of (91).

12.3. EOS based on data for τ_S $(\boldsymbol{P}, \boldsymbol{T})$.

Measured values of $\tau_S(P,T)$ allow us first to find the isobaric specific heat [*Dzhavadov*, 1986]

$$\ln \frac{C_P(P,S)}{T(P,S)} = \int\limits_0^P \left(\frac{\partial \tau_S}{\partial T}\right)_P dP + \ln \frac{C_P(0,S)}{T(0,S)}, \tag{131}$$

which is deduced from the identity $\partial^2 T / \partial P \partial S = \partial^2 T / \partial S \partial P$. The integral in (131) is taken over an adiabat, and the specific heat versus temperature, $C_P(T)$, for $P = 0$, is assumed to be known. Then, given a reference isotherm $V(P, T_0)$, from (14), we can find the thermal EOS in the form

$$V(P,T) = \int\limits_{T_0}^T \frac{\tau_S C_P}{T} dT + V(P, T_0). \tag{132}$$

Conversely, given the thermal EOS and $\tau_S(T)$ at $P = 0$, (14) gives $C_P(T)$ at $P = 0$, and thus, the caloric EOS can be determined.

Conclusion

We have reviewed thermodynamic properties of geomaterials necessary to study the thermodynamics of the deep interior of the Earth.

(1) In sections 2–5, it was shown that the determination of all the second-order thermodynamic parameters requires knowledge of values of three such parameters. In relation to EOS's, all the thermodynamic parameters were lumped into thermal and caloric types. A summary to finding of EOS's from experimental data was presented. The approaches directly based on measured thermodynamic characteristics can be formulated in the form of partial differential equations. Of 16 third-order thermodynamic parameters, only four (appropriately chosen) are independent. Attention is given to the compilation of a self-consistent database for minerals, relying on input data for α, K_S (or K_T), $(\partial K_S / \partial P)_T$, $(\partial \alpha / \partial T)_P$, $(\partial C_P / \partial T)_P$, and $(\partial K_S / \partial T)_P$.

(2) Each of the eight second-order parameters was analyzed separately, following the plan: the derivation of the identities between their P and T derivatives, the estimation of the intrinsic and extrinsic contributions to the temperature derivatives, useful simplifications of these relations and their consequences, and the explicit approximate dependences of the second-order parameters on pressure and temperature.

(3) In the analysis of thermal expansivity (section 6), the Birch formula for $\alpha = \alpha(P)$ at T (or S) = constant is generalized. It was shown that α in the lower mantle, calculated by the generalized formula, is sensitive to assumed values of the mixed $P - T$ derivative of the bulk modulus K_T, in the range of $dK_0'/dT \sim (0 - 4) \cdot 10^{-4}$ K^{-1}. The assignment of a value about $2 \cdot 10^{-4}$ K^{-1} for this derivative gives α in the lower mantle to be close to those by the (exponential) laws of *O. Anderson et al.* [1993] and *Chopelas and Boehler* [1992]. Based on these estimates and our analysis, we conclude that the coefficient of thermal expansion decreases along the hot lower-mantle adiabat (from $P = 0$ to $P = 1.35$ Mbar) by a factor of 4–5. Considering the O. Anderson power law for α, we stated strict conditions for the consistency of various assumptions regarding the EOS and parameters δ_T, K_T, K', and C_V and cleared up the consequencies of these assumptions. In many cases, these conditions are useful for a self-consistent thermodynamic analysis. For example, the power form of the Birch law, $K_T \sim V^b$ leads to $K' = $ constant, $K_T = K_T(V)$, $\delta_T = K' = $ constant, the Murnaghan EOS (41), and for $C_V = $ constant, $\alpha = \alpha(V)$. Various extrapolations of α to high temperatures at $P = 0$ show a great uncertainty in the resulting thermal expansivity (to 30–50% at $T \gtrsim 1500 - 2000$ K), which indicates that high-temperature measurements of α are very neeeded to improve the knowledge of α.

(4) The isobaric specific heat C_P under the lower-mantle conditions (section 7) decreases approximately 10% along the hot adiabat, from $P = 0$ to $P = 1.35$ Mbar. At low temperatures $T < \Theta$, the intrinsic anharmonicty competely prevails, but at $T > \Theta$, when $(\partial C_P / \partial T)_P$ is small, its contribution is only 15–30%.

(5) The difference between the thermal pressure model of O. Anderson and the Mie–Grüneisen EOS is emphasized (section 8). This model has two specific features: in general, its thermal pressure is linear in temperature, but the volume dependence of thermal pressure depends on the kind of material. From our estimation, at $T > \Theta$, the nonlinear terms in P_{th} contribute no more than 1–3%. In total, we refer to the existence of, at least, four models of thermal EOS: the Mie–Grüneisen (or more general anharmonic lattice) EOS, a model with various forms of the reference isotherm $P(V, T_0)$ and with a given $\alpha(P, T)$ dependence, the O. Anderson model mentioned above, and the formulation of type (28) with assumed temperature variations of the EOS parameters.

(6) In section 9, the Anderson–Grüneisen parameters δ_S and δ_T are analyzed in more detail. An explicit expression for $\delta_T(V)$ at T (or S) = constant was derived from the generalized formula of Birch. We find that, for $dK'_0/dT = 2.3 \cdot 10^{-4}$ K^{-1} (see the derivation of (3)), δ_T at the base of the mantle is almost half the value at $P = 0$.

(7) The adiabatic–isothermal transformation of bulk moduli are discussed in section 10. In addition to the previous considerations, the useful formula (98) was derived for the mixed derivative dK'_0/dT. Altogether, this parameter for various geomaterials is estimated by a value of the order of $(1 - 3) \cdot 10^{-4}$ K^{-1}.

From the analyzed temperature behavior of bulk moduli, we infer that the $\delta_V^T = K' - \delta_T$ and δ_V^S values at room temperature fall mostly between -4 and -1 and between -1 and 1, respectively. However, their high-temperature values are in the range from -1 to 1 for δ_V^T and from 0 to 1.5 for δ_V^S. The approximation $\delta_V^T \approx 0$ ($\delta_T \approx K'$ and $K_T = K_T(V)$) is justified for many but not all minerals.

In relation to the interpretation of seismic tomography data for the lower mantle, we found the following ranges of acceptable value for this largest layer of the Earth: $\delta_V^T \gtrsim 0.2$, $q \lesssim 0.8$, $\gamma \gtrsim 1.1$, $\delta_T \lesssim 3 - 3.3$, and $\delta_S \lesssim 1.9 - 2.2$ (provided that the thermal interpretation of these data is true).

The K_S values at high temperature, evaluated by the power law with δ_S = constant and by the O. Anderson enthalpy method have errors of the order of 2–6 and 1–3%, respectively. Thus, it is confirmed that the O. Anderson [1995] method is quite efficient.

(8) A number of identities for the Grüneisen parameter γ and its logarithmic derivative $q = (\partial \ln \gamma/\partial \ln V)_T$ were given in section 11. They show that the conditions C_V = constant or $C_V = C_V(T)$ lead to $\gamma = \gamma(V)$ or $\gamma = f(V)/C_V(T)$, respectively. Both these cases are compatible to the O. Anderson thermal pressure model, with $\tau = \alpha K_T$ = constant or $\tau = \tau(V)$. Any of the indicated conditions for C_V also gives $q = q(V)$ or $q =$ constant; moreover, from the inequality $0 \le q \le 1$, it

follows that $0 \le K' - \delta_T \le 1$ and vice versa. Thermodynamically estimated q values fall largely into the interval 0.5–2. This parameter generally decreases with pressure and temperature. In the derivative $(\partial \gamma/\partial T)_P$, the intrinsic anharmonicity prevails on the whole, suggesting a significant dependence of γ on temperature. In addition to many known expressions for $\gamma(V)$, we derived a new one based on the parameter $\lambda \equiv 1 - (\partial \ln \gamma T/\partial \ln V)_S \lessgtr 1$. The $\lambda = 0$ case is reduced to the Rice [1965] formula. Variation in λ in the interval of 0–1 (accordingly, $\delta_V^S \equiv \lambda(1 + \alpha\gamma T)^{-1}$ ranges approximately over the same interval for $\alpha\gamma T \ll 1$) appreciably affects the γ values at high compression.

(9) The identities and approximations for the adiabatic temperature gradient $\tau_S \equiv (\partial T/\partial P)_S$ were systematized. Our thermodynamic estimates of the Boehler parameter $n = (\partial \ln \tau_S/\partial \ln V)_T$ are close to his experimental results for olivine, quartz, and periclase. The uncertainty of the order of one in the estimated n is caused by errors in the used input thermodynamic data. In the derivative $(\partial \tau_S/\partial T)_P$, the intrinsic anharmonic contribution was found to dominate. When determining the EOS from data for τ_S, an important role is played by the relation of this parameter to specific heat.

Finally, in sections 6–8 and 10, we checked on the validity of the Mie–Grüneisen EOS used to evaluate α, C_P, τ, and K_S. Qualitatively, this EOS model correctly describes the $P - T$ behavior of the indicated parameters, but in general, it does not always provide a sufficiently high accuracy of the estimated values. For this reason (see also the inference (8) above), it is concluded that care must be exercised when applying this type of EOS in geophysics.

References

Agnon, A., and Bukowinski, M. S. T., Thermodynamic and elastic properties of a many-body model for simple oxides, Phys. Rev., B41, 7755–7766, 1990a.

Agnon, A., and Bukowinski, M. S. T., δ_S at high pressure and $d \ln V_S/d \ln V_P$ in the lower mantle, Geophys. Res. Lett., 17, 1149–1152, 1990b.

Ahrens, T. J., and Thomsen, L., Application of the fourth-

order anharmonic theory to the prediction of equations of state at high compressions and temperatures, *Phys. Earth Planet. Inter., 5,* 282–293, 1972.

Aidun, J., Bukowinsky, M. S. T., and Ross, M., Equations of state and metallization of CsJ, *Phys. Rev. Sect., B 29,* 2611–2621, 1984.

Al'tschuller, L. V., Use of shock waves in high pressure physics (in Russian), *Uspechi fiz. Nauk, 85,* 197–248, Engl. transl. In: *Sov. Phys. Usp., 8,* 52–91, 1965.

Anderson, D. L., A seismic equation of state, *Geophys. J. R. Astr. Soc., 13,* 9–30, 1967.

Anderson, D. L., A seismic equation of state: II. Shear properties and thermodynamics of the lower mantle, *Phys. Eartrh Planet. Inter., 45,* 307–323, 1987.

Anderson, D. L., Temperature and pressure derivatives of elastic constants with application to the mantle, *J. Geophys. Res., 83,* 4688–4700, 1988.

Anderson, D. L., *Theory of the Earth, Blackwell Scientific,* Boston Mass, 1989.

Anderson, D. L., and Anderson, O. L., The bulk modulus volume relationship for oxides, *J. Geophys. Res., 75,* 3494–3500, 1970.

Anderson, O. L., Derivation of Wachtman's equation for the temperature dependence of elastic moduli of oxide compounds, *Phys.Rev., 144,* 553–557, 1966a.

Anderson, O. L., Use of ultrasonic measurements at modest pressure to estimate high-pressure compression, *Phys. Chem. Solids, 27,* 547–565, 1966b.

Anderson, O. L., Equation for thermal expansivity in planetary interiors, *J. Geophys. Res., 72,* 3661–3668, 1967.

Anderson, O. L., Some remarks on the volume dependence of the Grüneisen parameter, *J. Geophys. Res., 73,* 5187–5194, 1968.

Anderson, O. L., A scaling law for K' for silicates with constant atomic mass, *Earth Planet. Sci. Letters, 20,* 73–76, 1973.

Anderson, O. L., The determination of the volume dependence of the Grüneisen parameter γ, *J. Geophys. Res., 79,* 1153–1155, 1974.

Anderson, O. L., The Hildebrand equation-of-state applied to minerals relevant to geophysics, *Phys. Chem. Miner., 5,* 33–51, 1979a.

Anderson, O. L., Evidence supporting the approximation const for the Grüneisen parameter of the Earth's lower mantle, *J. Geophys. Res., 84,* 3537–3542, 1979b.

Anderson, O. L., The high-temperature acoustic Grüneisen parameter in the Earth's interior, *Phys. Earth Planet. Inter., 18,* 221–231, 1979c.

Anderson, O. L., An experimental high-temperature thermal equation of state: bypassing the Grüneisen parameter, *Phys. Earth Planet. Inter., 22,* 173–183, 1980.

Anderson, O. L., Are anharmonicity corrections needed for temperature-profile calculations of interiors of terrestrial planets? *Phys. Earth Planet. Inter., 29,* 91–104, 1982.

Anderson, O. L., A universal thermal equation-of-state, *J. Geodynamics 1,* 185–214, 1984.

Anderson, O. L., The Earth's core and the phase diagram of iron, *Phil. Trans. R. Soc. Lond., A 306,* 21–35, 1986.

Anderson, O. L., Simple solid-state equations for materials of terrestrial planet interiors, In: *The Physics of the Planets,*

pp. 27–60, ed. by K. Runcorn, John Wiley, New York, 1988.

Anderson, O. L., The relationship betweenthe adiabatic bulk modulus and enthalpy for mantle-related minerals, *Phys. Chem. Miner., 16,* 559–569, 1989.

Anderson, O. L., Equations of State of Solids for Geophysics and Ceramic Science, N. Y., Oxford Univ. Press, 1995.

Anderson, O. L., Boehler, R., and Sumino, Y., Anharmonicity in the Equation of State at High Temperature for Some Geophysically Important Solids, In: *High-Pressure Research in Geophysics,* ed. by S. Aikimoto, M. H. Manghnani, 273–283, 1982.

Anderson, O. L., Chopelas, A., and Boehler, R., Thermal expansivity versus pressure at constant temperature: A re-examination, *Geophys. Res. Lett., 17,* (6), 685–688, 1990.

Anderson, O. L., and Goto, T., Measurement of elastic constants of mantle-related minerals at temperatures up to 1800 K, *Phys. Earth Planet. Inter., 55,* 241–253, 1989.

Anderson, O. L., Goto, T., and Isaak, D. G., The $dlnV_S/dlnV_P$ parameter in seismic tomography (abstract), *EOS Trans. Am. Geophys. Union, 68,* p. 1488, 1987.

Anderson, O. L., Isaak, D. G., and Oda, H., Thermodynamic parameters for six minerals at high temperature, *J. Geophys. Res., 96,* 18,037–18,046, 1991.

Anderson, O. L., Isaak, D. G., and Oda, H., High-Temperature Elastic Constant Data on Minerals Relevant to Geophysics, *Reviews of Geophysics, 30,* 57–90, 1992a.

Anderson, O. L., Oda, H., and Isaak, D. G., A model for the computation of thermal expansivity at high compression and high temperature: MgO as an example, *Geophys. Res. Lett., 19,* 1987–1990, 1992b.

Anderson, O. L., Kume, S., Ito, E., and Navrotsky, A., $MgSiO_3$ ilmenite: heat capacity, thermal expansivity, and enthalpy of transformation, *Phys. Chem. Miner., 16,* 239–245, 1988.

Anderson, O. L., and Nafe, J. E., The bulk modulus-volume relationship for oxide compounds and related geophysical problems, *J. Geophys. Res., 70,* 3951–3963, 1965.

Anderson, O. L., Oda, H., Chopelas, A., and Isaak, D. G., A Thermodynamic Theory of the Grüneisen Ratio at Extreme Conditions: MgO as an example, *Phys. Chem. Minerals 19,* 369–380, 1993.

Anderson, O. L., and Sumino, Y., The thermodynamic properties of the Earth's lower mantle, *Phys. Earth Planet. Inter., 23,* 314–331, 1980.

Anderson, O. L., and Suzuki, I., Anharmonicity of three minerals at high temperature: forsterite, fayalite, and periclase, *J. Geophys. Res., 88,* 3549–3556, 1983.

Anderson, O. L., and Yamamoto, S., Interrelationship of thermodynamic properties obtained by the piston-cylinder high-pressure experiments and RPR high temperature experiments for NaCl, In: *High Pressure Research in Mineral Physics,* Manghnani M. H., Syono Y. (eds), pp. 289–298, Center for Academic Publications, Tokyo, 1987.

Anderson, O. L., and Zou, K., Formulation of the thermodynamic functions for mantle minerals: MgO as an example, *Phys. Chem Minerals, 16,* 642–648, 1989.

Barron, T. H. K., A note on the Anderson-Grüneisen functions, *J. Phys., C12,* L155 -159, 1979.

Barton, M. A., and Stacey, F. D., The Grüneisen parameter at high pressure: a molecular dynamic study, *Phys. Earth Planet. Inter., 39,* 167–177, 1985.

Bassett, W. A., Takahashi, T., Mao, H.-K., and Weaver, J. S., Pressure-induced phase transformation in NaCl, *J. Appl. Phys., 34,* 319–325, 1968.

Berman, R. G., Internally consistent thermodynamic data for minerals in the system $Na_2O–K_2O–CaO–MgO–FeO–Fe_2O_3–Al_2O_3–SiO_2–TiO_2–H_2O–CO_2$, *J. Petrol., 29,* 445–522, 1988.

Bina, C. R., and Helffrich, G. R., Calculation of elastic properties from thermodynamic equation of state principles, *Annu. Rev. Earth Planet. Sci., 20,* 527–52?, 1992.

Birch, F., Elasticity and constitution of the Earth's interior, *J. Geophys. Res., 57,* 227–286, 1952.

Birch, F., The velocity of compressional waves in rocks to 10 kilobars, *J. Geophys. Res., 66,* part 2, 2199–2224, 1966.

Birch, F., Thermal expansion at high pressures, *J. Geophys. Res., 73,* 817–819, 1968.

Birch, F., Finite strain isotherm and velocities for single-crystal and policrystalline NaCl at high pressures and 300 K, *J. Geophys. Res., 83,* 1257–1268, 1978.

Birch, F., Equation of state and thermodynamic parameters of NaCl to 300 Kbar in the high-temperature domain, *J. Geophys. Res., 91,* 4949–4954, 1986.

Boehler, R., Adiabats of quartz, coesite, olivine and magnesium oxide to 50 Kbar and 1000 K and the adiabatic gradient in the Earth's mantle, *J. Geophys. Res., 87,* 5501–5506, 1982.

Boehler, R., Melting temperature and Grüneisen parameter of lithium, sodium and potassium versus pressure, *Phys. Rev., B27,* 6754–6762, 1983.

Boehler, R., Besson, J. M., Nicol, M., Nielsen, M., Itie, J. R., Weil, G., Johnson, S., and Grey, F., X-ray diffraction of γ-Fe at high temperatures and pressures, *J. Appl. Phys., 65,* 11,795–11,797, 1989.

Boehler, R., and Ramakrishnan, J., Experimental results of the pressure dependence of the Grüneisen parameter: a review, *J. Geophys. Res., 85,* 6996–7002, 1980.

Boisen, M. B., and Gibbs, G. V., A modelling of the structure and compressibility of quartz with a molecular potential and its transferability to crystalitite and coesite, *Phys. Chem. Miner.,* p. 123, 1993.

Born, M., and Huang, K., *Dynamic Theory of Crystal Lattices,* Oxford University Press, New York, 1954.

Brennan, B. J., and Stacey, F., A thermodynamically based equation of state for the lower mantle, *J. Geophys. Res., 84,* 5535–5539, 1979.

Brown, M., and Shankland, T. J., Thermodynamic parameters in the Earth as determined from seismic profiles, *Geophys. J. R. Astron. Soc., 66,* 579–596, 1981.

Bukowinski, M. S. T., and Wolf, G. H., Thermodynamically Consistent Decompression: Implications for Lower Mantle Composition, *J. Geophys. Res., 95,* 12,583–12,593, 1990.

Callen, H. B., *Thermodynamics,* New York, Wiley, 1960.

Campbell, A. J., and Heinz, D. L., A high-pressure test of Birch's law, *Science, 257,* 66–68, 1992.

Carter, W. J., Marsh, S. P., Fritz, J. N., and McQueen, R. B., The equation of state of selected materials for high-pressure reference, In: *Accurate Characterization of the High Pressure Environment,* ed. by E. C. Boyd, pp. 147–158, NBS special publ. 326, Washington D.C., 1971.

Catlow, C. R. A., and Price, G. D., Computer modelling of solid-state inorganic materials, *Nature, 347,* 243–248, 1990.

Catti, M., Theoretical computation of physical properties of mantle minerals, In: *Chemistry and Physics of Terrestrial Planets, Advances in Physical Geochemistry, vol. 6,* ed. by S. K. Saxena, pp. 224–250, Springer Verlag, New York, 1986.

Catti, M., Pavese, A., Apra, E., and Roetti, C., Quantum-mechanical Hartree-Fock study of calcite ($CaCO_3$) at variable pressure, and comparison with magnesite ($MgCO_3$), *Phys. Chem. Miner.,* p. 104, 1993.

Chopelas, A., Thermal properties of forsterite at mantle pressures derived from vibrational spectrometry, *Phys. Chem. Miner., 17,* 149–156, 1990a.

Chopelas, A., Thermal expansion, heat capacity, and entropy of MgO at mantle pressure, *Phys. Chem. Miner., 17,* 142–148, 1990b.

Chopelas, A., Thermal properties of β-Mg_2SiO_4 at mantle pressures derived from vibrational spectroscopy: Implications for the mantle at 400 km depth, *J. Geophys. Res., 96,* 11,817–11,829, 1991a.

Chopelas, A., Single crystal Raman spectra of forsterite, fayalite and monticellite, *Am. Mineral., 76,* 1101–1109, 1991b.

Chopelas, A., Sound velocities of MgO and $MgAl_2O_4$ to very high compression in the low mantle, *Terra abstracts,* V.S., Supplement No 1, p. 100, 1993.

Chopelas, A., and Boehler, R., Thermal expansivity in the lower mantle, *Geophys. Res. Lett., 19,* 1983–1986, 1992.

Chopelas, A., and Hofmeister, A. M., Vibrational Spectroscopy of Aluminate Spinels at 1 atm and of $MgAl_2O_4$ to over 200 kbar, *Phys. Chem. Miner., 18,* 279–293, 1991.

Chopelas, A., and Nicol, M. F., Pressure dependence to 100 kbar of the phonons of MgO at 90 and 295 K, *J. Geophys. Res., 94,* 8591–8597, 1982.

Chung, D. H., On the equation of state of high-pressure solid phases, *Earth Planet. Sci. Lett., 18,* 125–132, 1973.

Clark, S. R., Remarks on thermal expansion, *J. Geophys. Res., 74,* 731–732, 1969.

Cohen, R. E., Calculation of elasticity and high-pressure instabilities in corundum and stishovite with the potential induced breathing model, *Geophys. Res. Lett., 14,* 37–40, 1987a.

Cohen, R. E., Elasticity and equation of state of $MgSiO_3$ perovskite, *Geophys. Res. Lett., 14,* 1053–1056, 1987b.

D'Arco, F., Silvi, B., Roetti, C., and Orlando, R., Comparative Study of Spinel Compounds: A Pseudopotential Periodic Hartree-Fock Calculation of Mg_2SiO_4, Mg_2GeO_4, Al_2MgO_4 and Ga_2MgO_4, *J. Geophys. Res., 96,* 6107–6112, 1991.

Davies, G. F., *Quasi-harmonic finite strain equations of state of solids 34,* 1417–1429, 1973.

Davies, G. F., The estimation of elastic properties from analogue compounds, *Geophys. J. R. Astron. Soc., 44,* 625–647, 1976.

Dovesi, R., Pisani, C., Roetti, C., and Silvi, B., The elec-

tronic structure of α-quartz: A periodic Hartree-Fock calculation, *J. Chem. Phys., 86,* 6967–6971, 1987.

Duffy, T. S., and Ahrens, T. J., Sound velocities at high pressure and temperature and their geophysical inplications, *J. Geophys. Res., 97,* 4503–4520, 1992a.

Duffy, T. S., and Ahrens, T. J., Lateral variations in lower mantle seismic velocity, In: *High-Pressure Research: Application to Earth and Planetary Sciences,* ed. by Y. Syono and M. H. Manghnani, Terra, Washington, (in press), 1992b.

Duffy, T. S., and Ahrens, T. J., Thermal expansion of mantle and core materials at very high pressures, *Geophys. Res. Letters, 20,* 1103–1106, 1993.

Duffy, T. S., and Anderson, D. L., Seismic velocities in mantle minerals and the mineralogy of the upper mantle, *J. Geophys. Res., 94,* 1895–1912, 1989.

Dzhavadov, L. N., Determination of thermodynamic functions from measurements of the adiabatic temperature gradient under pressure (in Russian), *Fiz. tverdogo tela, 27,* 1106–1108, 1986 (in Russian).

Fabrichnaya, O. B., and Kuskov, O. L., Constitution of the mantle. 1. Phase relations in the FeO–MgO–SiO$_2$ system at 10–30 GPa, *Phys. Earth Planet. Inter., 69,* 56–71, 1991.

Fei, Y., Mao, H.-K., and Mysen, B. O., Experimental Determination of Element Partitioning and Calculation of Phase Relations in the MgO–FeO–SiO$_2$ System at High Pressure and High Temperature, *J. Geophys. Res., 96,* 2157–2169, 1991.

Fei, Y., Mao, H.-K., Shu, J., and Hu, J., $P-V-T$ Equation of State of Magnesiowüstite (Mg$_{0.6}$Fe$_{0.4}$)O, *Phys. Chem. Miner., 18,* 416–422, 1992a.

Fei, Y., Mao, H.-K., Parthasarathy G., Bassett W. A., and Ko J., Simultaneous high $P-T$ X-ray diffraction study of β-(Mg,Fe)$_2$SiO$_4$ to 26 GPa and 900 K, *J. Geophys. Res., 97,* 4489–4495, 1992b.

Fei, Y., and Saxena, S. K., A Thermodynamical Data Base for Phase Eqilibria in the System Fe–Mg–Si–O at High Pressure and Temperature, *Phys. Chem. Miner., 13,* 311–324, 1986.

Fei, Y., and Saxena, S. K., An equation for the heat capacity of solids, *Geochim. Cosmochim. Acta, 51,* 251–254, 1987.

Fei, Y., Saxena, S. K., and Navrotsky, A., Internally consistent thermodynamic data and equilibrium phase relations for compounds in the system MgO–SiO$_2$ at high pressures and high temperatures, *J. Geophys. Res., 95,* 6915–6928, 1990.

Finger, L. W., and Hazen, R. M., *J. Appl. Phys., 49,* 5823, 1978.

Finger, L. W., Hazen, R. M., Zhang, J. M., and Ko, J., Effects of Fe on the crystal chemistry β-(Mg,Fe)$_2$SiO$_4$, *EOS Trans. AGU, 71,* p. 524, 1990.

Fiquet, G., Gillet, Ph., and Richet, P., Anharmonic contributions to the heat capacity of minerals at high temperatures, Application to Mg$_2$GeO$_4$, Ca$_2$GeO$_4$, MgCaGeO$_4$ olivines, *Phys. Chem. Miner., 18,* 469–479, 1992.

Frisillo, A. L., and Barsch, G. R., Measurement of single-crystal elastic constants of bronzite as a function of pressure and temperature, *J. Geophys. Res., 77,* 6360–6384, 1972.

Fujisawa, H., No Olivine in the Mantle? (abstract), *Trans. EOS, 68,* 409 pp., 1987.

Fürth, R., On the equation of state of solids, *Proc. R. Soc., A183,* 87–110, London, 1944.

Furukawa, G. T., Douglas, T. B., McCoskey, R. E., and Ginning, D. C., Thermal properties of aluminium oxide from 0 to 1200 K, *J. Res. Natl. Bur. Stand., 57,* 121–131, 1968.

Gillet, Ph., Guyot, F., and Malézieux, J. M., High pressure and high temperature Raman spectroscopy insights on anharmonicity, *Phys. Earth Planet. Inter., 58,* 141–154, 1989.

Gillet, Ph., Le Cleach, A., and Madon, M., High-temperature Raman spectroscopy of the SiO$_2$ and GeO$_2$ polymorphs: anharmonicity and thermodynamic properties at high temperature, *J. Geophys. Res., 95,* 21,635–21,655, 1990.

Gillet, Ph., Richet, P., Guyot, F., and Fiquet, G., High temperature thermodynamic properties of forsterite, *J. Geophys. Res., 96,* 11,805–11,816, 1991.

Goto, T., Yamamoto, S., Ohno, I., and Anderson, O. L., Elastic constants of corundum up to 1825 K, *J. Geophys. Res., 94,* 7588–7602, 1989.

Graham, E. K., Sopkin, S. M., and Resley, W. E., Elastic constants of fayalite, Fe$_2$SiO$_4$ and the olivine solution series (abstract), *EOS Trans. AGU, 63,* p. 1090, 1982.

Grüneisen, E., The state of solids, In: *Hanbuch der Physik,* p. 10, 1926.

Gupta, G. M., *J. Geophys. Res., 88,* 4304–4312, 1983.

Hardy, R. J., Temperature and pressure dependence of intrinsic anharmonic and quantum corrections to the equation of state, *J. Geophys. Res., 85,* 7011–7015, 1980.

Hazen, R. J., Effects of temperature and pressure on the crystal structure of forsterite, *Am. Mineral., 61,* 1280–1293, 1976.

Hazen, R. J., Perovskites, *Sci. Amer.,* June, 74–81, 1988.

Hazen, R. J., and Finger, L. W., High-pressure crystal chemistry of andradite and pyrope: revised procedures for high-pressure diffraction experiments, *Am. Miner., 74,* 352–359, 1989.

Hemley, R. J., Jackson, M. D., and Gordon, R. G., First principle theory of equations of state at high pressures and high temperatures: Application to MgO, *Geophys. Res. Lett., 12,* 247–250, 1985.

Hemley, R. J., Jackson, M. D., and Gordon, R. G., Theoretical study of the structure, lattice dynamics, and equations of state of perovskite-type MgSiO$_3$ and CaSiO$_3$, *Phys. Chem. Miner., 14,* 2–12, 1987.

Hofmeister, A. M., Single-crystal absorption and reflection infrared spectroscopy of forsterite and fayalite, *Phys. Chem. Miner., 14,* 499–513, 1987.

Hofmeister, A. M., Calculation of Bulk Modulus and Its Pressure Derivatives from Vibrational Frequencies and Mode Grüneisen Parameters: Solids with Cubic Symmetry or One Nearest-Neighbor Distance, *J. Geophys. Res., 96,* 16,181–16,203, 1991a.

Hofmeister, A. M., Pressure derivatives of the bulk modulus, *J. Geophys. Res., 96,* 21,893–21,907, 1991b.

Hofmeister, A. M., Xu, J., Mao, H.-K., Bell, P. M., and Hoering, T. C., Thermodynamics of Fe–Mg olivines at man-

tle pressure: mid- and far-infrared spectroscopy at high pressure, *Am. Miner.*, *74*, 281–306, 1989.

Iishi, K., Lattice dynamics of forsterite, *Am. Miner.*, *63*, 1198–1208, 1978.

Irvine, R. D., and Stacey, F. D., Pressure dependence of the thermal Grüneisen parameter, with application to the Earth's lower mantle and outer core, *Phys. Earth Planet. Inter.*, *11*, 157–165, 1975.

Isaak, D. G., The mixed P, T derivatives of elastic moduli and implications on extrapolating throughout the Earth's mantle, *Phys. Earth Planet. Inter.*, *80*, 37–48, 1993.

Isaak, D. G., and Anderson, O. L., The relationship between shear and compressional velocities at high pressures: reconciliation of seismic tomography and mineral physics, *Geophys. Res. Lett.*, *19*, 741–744, 1992.

Isaak, D. G., Anderson, O. L., and Cohen, R. E., The relationship between shear and compressional velocities at high pressures: reconciliation of seismic tomography and mineral physics, *Geophys. Res. Lett.*, *19*, 741–744, 1992.

Isaak, D. G., Anderson, O. L., and Goto, T., Measured elastic modules of single-crystal MgO up to 1800 K, *Phys. Chem. Miner.*, *16*, 703–704, 1989a.

Isaak, D. G., Anderson, O. L., and Goto, T., Elasticity of single-crystal forsterite measured to 1700 K, *J. Geophys. Res.*, *94*, 5895–5906, 1989b.

Isaak, D. G., Cohen, R. E., and Mehl, M. J., Calculated elastic and thermal properties of MgO at high pressures and temperatures, *J. Geophys. Res.*, *95*, 7055–7067, 1990.

Jackson, I., and Niesler, H., The elasticity of periclase to 3 GPa and some geophysical implications, In: *High Pressure Research in Geophysics*, ed. by S. Akimoto and M. H. Manghnani, pp. 93–133, Center for Academic Publishing, Tokyo, 1982.

Jeanloz, R., Mineral and melt physics, A summary of research in the Unated States, 1979–1982, *Rev. Geophys.*, *21*, 1487–1503, 1983.

Jeanloz, R., Shock-wave equation of state and finite-strain theory, *J. Geophys. Res.*, *94*, 5873–5886, 1989.

Jeanloz, R., and Knittle, E., Density and composition of the lower mantle, *Philos. Trans. R. Soc. London, Ser. A*, *328*, 377–389, 1989.

Jeanloz, R., and Thompson, A. B., Phase transitions and mantle discontinuities, *Rev. Geophys.*, *21*, 51–74, 1983.

Jones, L., High-temperature behavior of the elastic moduli of LiF and NaF: Comparison with MgO and CaO, *Phys. Earth Planet. Inter.*, *13*, 105–118, 1976.

Kalinin, V. A., On the universal equation of state, Izv. Akad. Nauk SSSR, *Fiz. Zemli*, (4), 16–23, 1972 (in Russian).

Kalinin, V. A., and Pankov, V. L., Equations of state of stishovite, coesite and quartz, Iz. Akad. Nauk SSSR, *Fiz. Zemli*, (3), 3–15, 1972 (in Russian).

Kalinin, V. A., Pankov, V. L., and Kalachnikov, A. A., Comparison of two methods of computing complete phase diagrams for the MgO-SiO₂ system, *Izv. Earth Phys.*, *3*, 88–89, 1991 (in Russian).

Kelly, D. C., *Thermodynamics and statistical physics*, Academic Press, New York, 1973.

Kieffer, S. W., Thermodynamics and lattice vibrations of minerals: 1,2,3,4, *Rev. Geophys. Space Phys.*, *18*, 1–19, 1979a, 20–24, 1979b, 35–59, 1979c, 862–886, 1980.

Knopoff, L., Equations of state of solids at moderately high pressures, In: *High Pressure Physics and Chemistry, Vol.1*, ed. by R. S. Bradley, pp. 227–245, Academic, San Diego, Calif., 1963.

Knopoff, L., and Shapiro, J. N., Comments on the interrelationships between Grüneisen parameter and shock and isothermal equations-of-state, *J. Geophys. Res.*, *74*, 1439–1445, 1969.

Kuskov, O. L., and Galimzyanov, R., Thermodynamics of stable mineral assemblages of the mantle transition zone, In: *Chemistry and Physics of the Terrestrial Planets*, ed. by S. K. Saxena, pp. 310–361, Springer-Verlag, New York, 1986.

Kuskov, O. L., and Panferov, A. B., Phase diagrams of the FeO–MgO–SiO₂ system and the structure of the mantle discontinuities, *Phys. Chem. Miner.*, *17*, 642–653, 1991.

Kuskov, O. L., Panferov, A. B., Fabrichnaya, O. B., Galimzyanov, R. F., and Truskinovskii, L. M., Petrological–geophysical model of the mantle transition zone, In: *Planetnaya kosmogoniya i nauka o Zemle (Planetary Cosmogony and Earth Sciences)*, ed. by V. A. Magnitsky, Nauka, Moscow, 1989 (in Russian).

Leibfried, G., and Ludwig, W., Theory of anharmonic effects in crystals, *Solid State Phys.*, *12*, 275–444, 1961.

Leliva-Kopystynski, J., Equations of state in geophysics and in planetary physics, In: *High-Pressrue Equations of State: Theory and Applications, Proc. Int. "E. Fermi" 1989 Summer School*, ed. by S. Eliezer, R. A. Ricci, pp. 439–464, North-Holland, Amsterdam, 1991.

Liebermann, R. C., Li, B., Gwanmesia, G. D., Rigden, S. R., and Jackson, I., Velocities of high-pressure phases of mantle minerals and seismic models of the mantle transition zone, *Terra abstracts, V. 5*, Supplement No.1, p. 102, 1993.

Liu, M., and Liu, L., Bulk moduli of wüstite and periclase: a comparative study, *Phys. Earth Planet. Inter.*, *45*, 273–279, 1987.

Mao, H.-K., Velocity-density systematics and its implications for the iron content of the mantle, *J. Geophys. Res.*, *79*, 5447–5450, 1974.

Mao, H.-K., and Bell, P. M., Equation of state of MgO and ε–Fe under static pressure conditions, *J. Geophys. Res.*, *84*, 4533–4536, 1979.

Mao, H.-K., Hemley, R. J., Fei, Y., Shu, J. F., Chen, L. C., Jephcoat, A. P., and Wu, Y., Effect of Pressure, Temperature, and Composition on Lattice Parameters and Density of (Mg,Fe)SiO₃–Perovskites to 30 GPa, *J. Geophys. Res.*, *96*, 8069–8079, 1991.

Mao, H.-K., Xu, J., and Bell, P. M., Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic pressure, *J. Geophys. Res.*, *91*, 4673–4676, 1986.

Matsui, M., Molecular dynamics study of MgSiO₃ perovskite, *Phys. Chem. Miner.*, *16*, 234–238, 1988.

Matsui, M., Molecular dynamics study of the structural and thermodynamic properties of MgO crystal with quantum correction, *J. Chem. Phys.*, *91*, 489–494, 1989.

Matsui, M., Akaogi, M., and Matsumoto, T., Computational model of the structural and elastic properties of the ilmenite and perovskite phases of MgSiO₃, *Phys. Chem. Miner.*, *14*, 101–106, 1987.

Matsui, M., and Price, G. D., Simulation of the pre-melting behavior of MgSiO₃ perovskite at high pressures and temperatures, *Nature, 351,* 735–737, 1991.

McMillan, P. F., and Ross, N. L., Heat capacity calculations for Al₂O₃ corundum and MgSiO₃ ilmenite, *Phys. Chem. Miner., 14,* 225–234, 1987.

McQueen, R. G., Shock Waves in Condensed Media: their Properties and the Equation of State of Materials Derived from them, In: *High-Pressrue Equations of State: Theory and Applications, Proc.Int. "E. Fermi" 1989 Summer School,* ed. by S. Eliezer, R. A. Ricci, pp. 101–216, North-Holland, Amsterdam, 1991.

McQueen, R. G., Marsh, S. P., Taylor, J. W., Fritz, J. N., and Carter, W. J., The equation of state from shock wave studies, In: *High-Velocity Impact Phenomena,* ed. by R. Kinslow, pp. 293–417, Academic, New York, 1970.

Molodets, A. M., The Volume and Temperature Dependence of the Grüneisen parameter, Doctoral Dissertation, Institute of Chemical Physics Ploblems, 1998 (in Russian).

Morse, P.M., *Thermal physics,* Second ed., Benjamin, New York, 1969.

Mulargia, F., Is the common definition of the Mie-Grüneisen equation of state inconsistent? *Geophys. Res. Lett., 4,* 590–593, 1977.

Mulargia, F., and Boschi, E., The Problem of the Equation of State in the Earth's Interior, In: *Proc. Int. "E. Fermi" 1979 Summer School,* Dziewonski A., Boschi E. (eds), pp. 337–367, North-Holland, Amsterdam, 1980.

Mulargia, F., and Broccio, F., On the reduction of experimental thermodynamic data to constant configuration, *Boll. Geofis. Teor. Applicata, 25,* 113–118, 1983.

Mulargia, F., Broccio, F., and Dragoni, M., On the temperature dependence of the Grüneisen function, *Boll. Geofis. Applicata, 26,* 229–236, 1984.

Murnaghan, F.D., *Finite deformation of an elastic solid,* Wiley, New York, 1951.

Navrotsky, A., and Akaogi, M., The α, β, τ phase relations for Fe₂SiO₄–Mg₂SiO₄ and Co₂SiO₄–Mg₂SiO₄: calculations of phase diagrams, thermochemical data and geophysical applications, *J. Geophys. Res., 89,* 10,135–10,140, 1984.

Pankov, V. L., On volume dependence of the Grüneisen parameter, *Report on the International High-Pressure Conference,* Mischkolz University, Hungary, p. 24–29, October, 1983.

Pankov, V. L., Perovskite model of the lower mantle, in: *Fizika i vnutrennee stroenie Zemli (Physics and Internal Structure of the Earth),* ed. by V. A. Magnitsky and V. N. Zharkov, Nauka, Moscow, 1989.

Pankov, V. A., On the negative thermal expansivity, Fiz. Zemli, (6), 106–111, 1992 (in Russian).

Pankov, V. L., and Ullmann, W., A comparative method for various approaches to the isothermal equations of state, *PAGEOPH, 117,* 1001–1010, 1979a.

Pankov, V. L., and Ullmann, W., On the interrelation between adiabat and Hugoniot curves through Grüneisen parameter, *Gerlands Beitr. Leiptig, 88,* 433–452, 1979b.

Pankov, V. L., Kalachnikov, A. A., and Kalinin, V. A., Phase diagram of the FeO-SiO₂ system, Izv. Earth Physics, (7), 3–11, 1991 (in Russian).

Pankov, V. L., Kalinin, V. A., and Kalachnikov, A. A., Phase diagrams of the MgO-SiO₂ and FeO-SiO₂ systems and nature of the mantle, Fiz. Zemli, (6), 17–29, 1996.

Pankov, V. L., Bayuk, I. O., Bubnova, N. Ya., Kalachnikov, A. A., and Nasimov, R. M., *Thermodynamic (thermal and caloric) properties of mantle minerals,* URL: http//www.scgis.ru/russian/cp1251 sdb_1.html (in Russian).

Pankov, V. L., Kalachnikov, A. A., and Bubnova, N. Ya., Equations of state of silicate perovskite and magnsiowustite, *Fiz. Zemli,* (11), 1998 (in Russian).

Pitzer, K. S., and Brewer, L., (eds), *Thermodynamics,* McGraw-Hill, New York, 1961.

Price, G. D., Wall, A., and Parker, S. C., The properties and behavior of mantle minerals: a computer simulation approach, *Philos. Trans. R. Soc. London Ser., A328,* 391–407, 1989.

Quareni, F., and Mulargia, F., The validity of the common approximate expressions for the Grüneisen parameter, *Geophys. J., 93,* 505–519, 1988.

Quareni, F., and Mulargia, F., The Grüneisen parameter and adiabatic gradient in the Earth's interior, *Phys. Earth Planet. Inter., 55,* 221–233, 1989.

Reynard, B., and Price, G. D., Thermal expansion of mantle materials at high pressure – a theoretical study, *Geophys. Res. Lett., 17,* 689–693, 1990.

Reynard, B., Price, G. D., and Gillet, Ph., Thermodynamic and anharmonic properties of forsterite, α–Mg₂SiO₄: computer modelling versus high-pressure and high-temperature measurements, *J. Geophys. Res., 97,* 19,791–19,802, 1992.

Rice, M. H., Pressure-volume relations for the alkali metals from shock-wave measurements, *J. Phys. Chem. Solids, 26,* 483–492, 1965.

Richet, P., and Fiquet, G., High-temperature heat capacity and premelting of minerals in the system MgO–CaO–Al₂O₃–SiO₂, *J. Geophys. Res., 96,* 445–456, 1991.

Richet, P., Gillet, Ph., and Fiquet, G., Thermodynamic properties of minerals: macroscopic and microscopic approaches, *Adv. Phys. Geochem., 10,* 98–131, 1992.

Richet, P., Mao, H.-K., and Bell, P. M., Bulk moduli of magnesiowüstite from static compression measurements, *J. Geophys. Res., 94,* 3037–3045, 1989.

Richet, P., Xu, J.-A., and Mao, H.-K., Quasi-hydrostatic compression of ruby to 500 kbar, *Phys. Chem. Miner., 16,* 207–211, 1988.

Robie, R. A., Hemingway, B. S., and Fisher, J. R., Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (105 Pascals) pressure and at high temperatures, *US Geol. Surv. Bull.,* (1452), 456 pp, 1978.

Saxena, S. K., Assessment of thermal expansion, bulk modulus, and heat capacity of enstatite and forsterite, *J. Phys. Chem. Solids, 49,* 1233–1235, 1988.

Saxena, S. K., Assessment of bulk modulus, thermal expansion and heat capacity of minerals, *Geochim. Cosmochim. Acta, 53,* 785–789, 1989.

Saxena, S. K., and Zhang, Z., Thermochemical and Pressure-Volume-Temperature Systematics of Data on Solids, Examples: Tungsten and MgO., *Phys. Chem. Miner., 17,* 45–51, 1990.

Schankland, T. J., and Chung, D. H., General relationships among sound speeds, *Phys. Earth Planet. Inter.,* *8,* p. 121, 1974.

Silvi, B., Bouaziz, A., and D'Arco, Ph., Pseudo-potential periodic Hartree-Fock study of Mg_2SiO_4 polymorphs: olivine, modified spinel and spinel, *Phys. Chem. Miner.,* p. 333, 1993.

Smith, C. S., and Cain, L. S., Temperature derivatives at constant volume of the elastic constants of the alkali halides, *J. Phys. Chem. Solids, 41,* 199–203, 1980.

Sobolev, S. V., and Babeyko, A. Yu., Phase transition in the continental lower crust and its seismic structure, In: *Properties and Processes of the Earth's lower crust,* Mereu et al. (eds), Geophys. Monogr., 51, IUGG, Vol. 6, 1989.

Spetzler, H., Equation of state of poly-crystalline and single-crystal MgO to 8 kilobars and 800 K, *J. Geophys. Res., 75,* 2073–2087, 1970.

Stacey, F. D., Application of thermodynamics to fundamental Earth Physics, *Geophys. Surveys, 3,* 175–204, 1977a.

Stacey, F. D., A thermal model of the Earth, *Phys. Earth Planet. Inter., 15,* 341–348, 1977b.

Stacey, F. D., Finite strain theories and comparisons with seismological data, *Gophys. Surveys, 4,* 189–232, 1981.

Stacey, F., *Physics of the Earth,* 3rd ed., Brookfeld Press, Brisbane, Australia, 1992.

Stacey, F., *Theory of Thermal and Elastic Properties of the Lower Mantle and Core.* Manuscript, Phys. Dept, The University of Queensland, Brisbane 4072, Australia, 1994.

Sumino, Y., and Anderson, O. L., Elastic constants of minerals, In: *Handbook of Physical Properties of Rocks, VIII,* ed. by R. S. Carmichael, pp. 39–137, CRC, Boca Raton, Fl, 1984.

Sumino, Y., Anderson, O. L., and Suzuki, I., Tmeperature coefficients of single crystal MgO between 80 and 1300 K, *Phys. Chem. Miner., 9,* 38–47, 1983.

Suzuki, I., Thermal expansion of periclase and olivine and their anharmonic properties, *J. Phys. Earth, 23,* 145–159, 1975a.

Suzuki, I., Cell parameters and linear thermal expansion coefficients of orthopyroxenes, *J. Seismol. Soc. Jpn., 28,* 1–9, 1975b.

Thomsen, L., On the fourth-order anharmonic equation of state of solids, *J. Phys. Chem. Solids, 31,* 2003–2016, 1970.

Thomsen, L., Equations of State and the Interior of the Earth, In: *Mantle and Core in Planetary Physics (Proc. Int. School of Physics "Enriko Fermi"),* J. Coulomb, M. Caputo (eds), pp. 94–133, New York, 1971.

Ullmann, W., and Pankov. V. L., A new structure of the equation of state and its application in high-pressure physics and geophysics, Veröffentliche des ZIPE, Potsdam, No. 41, 1976.

Ullmann, W., and Pankov, V. L., Application of the Equation of State to the Earth's Lower Mantle, *Phys. Earth Planet. Inter., 22,* 194–203, 1980.

Vassiliou, M. S., and Ahrens, T. J., Hugoniot equation of state of periclase to 200 GPa, *Geophys. Res. Lett., 8,* 229–232, 1981.

Vinet, P., Ferrante, J., Rose, J. H., and Smith, J. R., Compressibility of solids, *J. Geophys. Res., 92,* 9319–9325, 1987.

Wall, A., Parker, S. C., and Watson, G. W., The extrapolation of elastic moduli to high pressure and temperature, *Phys. Chem. Miner., 20,* 69–75, 1993.

Wall, A., and Price, G. D., Computer simulation of the structure, lattice dynamics and thermodynamics of ilmenite-type $MgSiO_3$, *Am. Miner., 73,* 224–231, 1988.

Wall, A., Price, G. D., and Parker, S. C., A computer simulation of the structure and elastic properties of $MgSiO_3$ perovskite, *Mineral. Mag., 50,* 693–707, 1986.

Wallace, D. C., *Thermodynamics of crystals,* John Wiley, New York, 1972.

Walzer, U., The application of a pseudopotential approach to the physics of binary intermetallic compounds, *High Temperature–High Pressure, 24,* 23–34, 1992.

Watanabe, H., Thermochemical properties of synthetic high-pressure compounds relevant to the Earth's mantle, In: *High-Pressure Research in Geophysics,* Akimoto S. and Manghnani M.H. (eds). Center Acad. Publ. Japan, Tokyo, 441–464, 1982.

Webb, S. L., Elasticity of the upper mantle orthosilicates, olivine and garnet, *Phys. Chem. Miner., 16,* 684–692, 1989.

Webb, S. L., and Jackson, I., The anomalous pressure dependence of the elastic moduli for single-crystal orthopyroxene (abstract), *EOS Trans. AGU, 66,* p. 371, 1985.

Weidner, D. J., and Hamaya, N., Elastic properties of the olivine and spinel polymorphs of Mg_2GeO_4 and elevation of elastic analogues, *Phys. Earth Planet. Inter., 33,* 275–283, 1983.

White, G. K., and Roberts, R. B., Thermal expansion of reference materials: Tungsten and α-Al_2O_3, *High Temperature–High Pressure, 15,* 321–328, 1983.

Will, G., Hoffman, W., Hinze, E., and Lauterjung, J., The compressibility of forsterite up to 300 kbar measured with synchrotron radiation, *Physica, 139, 140B,* 193–197, 1986.

Williams, Q., Jeanloz, R., and McMillan, P., Vibrational spectrum of $MgSiO_3$ perovskite: zero-pressure Raman and mid-infrared spectra to 27 GPa, *J. Geophys. Res., 92,* 8116–8128, 1987.

Wolf, G. H., and Bukowinski, M. S. T., Theoretical study of the structural properties and equations of state of $MgSiO_3$ and $CaSiO_3$ perovskites: Implications for lower mantle composition, In: *High-Pressure Research in Mineral Physics, Geophys. Monogr. Ser., Vol. 39,* ed. by M. H. Manghnani and Y. Syono, pp. 313–331, AGU, Washington, D.C., 1987.

Wolf, G. H., and Bukowinski, M. S. T., Variational stabilization of the ionic charge densities in the electronic-gas theory of crystals: Application to MgO and CaO, *Phys. Chem. Miner., 15,* 209–220, 1988.

Yagi, T., Akaogi, Shimamura, O., and Akimoto, S., High pressure and high temperature equation of state of majorite, In: *High Pressure Research in Mineral Physics,* ed. by M. Manghnani and Y. Syono, AGU, Washington, D.C., 141–147, 1987.

Yeganeh-Haeri, A., and Vaughan, M. T., Single-crystal elastic constants of olivine (abstract), *EOS Trans. AGU, 65,* p. 282, 1984.

Yoneda, A., Pressure derivatives of elastic constants of single crystal MgO and MgAl$_2$SiO$_4$, *J. Phys. Earth, 38,* 19–55, 1990.

Zharkov, V. N., *Internal Structure of Earth and Planets,* Harwood, New York, 436 pp., 1986.

Zharkov, V. N., Thermodynamic of the mantle, Izv. Akad. Nauk SSSR, *Fiz. Zemli,* (9), 1414–1419, 1959.

Zharkov, V. N., Report on the International Conference Physical–Chemical Studies in the Earth Sciences, Joint Institute of Physics of the Earth, Moscow, 1997.

Zharkov, V. N., and Kalinin, V. A., *Equations of State of Solids at High Pressures and Temperatures,* 257 pp., Consultants Bureau, New York, 1971.