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The Gibbs energy formulation of the α , β , and γ forms of Mg_2SiO_4 using Grover, Getting and Kennedy's empirical relation between volume and bulk modulus

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Abstract The empirical linear relation between volume and logarithm of bulk modulus of a material, discovered by Grover, Getting and Kennedy is taken as the basis for our equation of state. Using the latest experimental information on the adiabatic bulk modulus, the equation of state is applied to the three polymorphs of Mg_2SiO_4 to develop a consistent dataset of their thermodynamic properties in the temperature range of 200–2273 K and a pressure range of 0.1 MPa–30 GPa. The results imply that the bulk sound velocity contrast $(v^\beta - v^\alpha)/v^\alpha$ increases with temperature along the α – β phase boundary and reaches the value 8.9% at 13.5 GPa, a pressure equivalent to 410 km depth in the Earth. The bulk sound velocity contrast $(v^\gamma - v^\beta)/v^\beta$ decreases with temperature along the β – γ phase boundary and becomes less than 0.7% at temperatures and pressures equivalent to those associated with the 520-km seismic discontinuity in the Earth.

Key words Thermal expansivity · Bulk modulus · Sound velocity · Equation of state · Olivine

Introduction

Recently, we have developed an equation of state based on the linear relationship between volume and logarithm of isothermal bulk modulus discovered by Grover et al. (1973). We applied this equation of state to the substance MgO and came to the conclusion that thermodynamic properties at high pressure and temperature

can be accurately predicted using thermodynamic data at 0.1 MPa pressure only, see Jacobs and Oonk (2000a, b). An important characteristic of the equation of state is that it has just two substance-dependent, adjustable parameters.

We are currently in the process of constructing a database founded on the new equation of state. The emphasis is on the various materials that make their appearance in the system MgO–FeO–SiO₂–Al₂O₃–CaO, which is of great relevance from a geodynamic point of view. The work involves a critical assessment of the complete collection of available experimental data. Here, we present the assessment of the three polymorphs of Mg_2SiO_4 , which are the olivine form (α), the wadsleyite form (β) and the ringwoodite form (γ).

Several earlier studies were undertaken to develop an internally consistent database of the system MgO–SiO₂. These studies include Fei and Saxena (1986), Saxena and Chatterjee (1986), Bina and Wood (1987) and Fei et al. (1990). A study of the complex system Fe–Mg–Si–O has been carried out by Fabrichnaya (1998). In our work we have incorporated new sources of experimental information on thermal expansivity and bulk modulus. New data on the thermal expansivity of α - Mg_2SiO_4 became available through the experiments of Gillet et al. (1991) and Bouhifd et al. (1996), which both deviate from the earlier data by Kajiyoshi (1986). New bulk modulus data are from Yoneda and Morioka (1992), Duffy et al. (1995), Li et al. (1996) and Zha et al. (1996) for the olivine form, from Li et al. (1998) for the wadsleyite form and from Jackson et al. (2000) for the ringwoodite form.

Hereafter, we first present a short description of the new equation of state, its experimental background, and its function as the starting point for calculating Gibbs energies. Next, considerable attention is given to the assessment of the available data at 0.1 MPa pressure. Thereafter the significance of the result is checked by comparing experimental data and calculated values for properties at high pressure. Finally, and as an application of the thermodynamic result, attention is given to sound velocities.

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The equation of state

From shock-wave and static compression measurements on a variety of metals, Grover et al. (1973) found a nearly precise linear relation between the logarithm of bulk modulus and volume – up to volume changes of 40%. We have demonstrated (Jacobs and Oonk (2000a, b)) that this relationship is useful to predict the thermochemical and thermophysical properties of MgO at high pressures and temperatures. In short, the derivation of the equation of state is as follows. We write Grover's relationship as:

$$V_m^0(T) = V_m^0(T_0) + b \cdot \ln\left(\frac{K^0(T)}{K^0(T_0)}\right), \quad (1)$$

where V_m^0 denotes molar volume (expressed in $\text{m}^3 \text{mol}^{-1}$), K the isothermal bulk modulus, T_0 a reference temperature and the superscript 0 refers to standard pressure (0.1 MPa = 1 bar). In Eq. (1), b is a material-dependent constant. The isothermal bulk modulus, which is the inverse of the isothermal compressibility, is defined as

$$K = -V \left(\frac{\partial P}{\partial V} \right)_T, \quad (2)$$

and differs from the definition of bulk modulus used in classical mechanics $K = -V_0(\partial P/\partial V)_T$, in which V_0 is a reference volume.

In the construction of an equation of state we have adopted the hypothesis that Eq. (1) is valid at any pressure, that is, we have made the assumption that Grover's relationship is valid not only for isobaric heating but also for isothermal compression. Dropping the subscript m in volume, the isothermal bulk modulus is written as:

$$\left(\frac{K}{\text{Pa}} \right) = -V \left(\frac{\partial P}{\partial V} \right)_T \times \frac{1}{\text{Pa}} = K^0(T_0) \times \exp\left(\frac{V - V^0(T_0)}{b}\right). \quad (3)$$

The solution of this differential equation is a power series in V :

$$\frac{P}{\text{Pa}} = \frac{P^0}{\text{Pa}} - K^0(T_0) \left\{ \exp\left(-\frac{V^0(T_0)}{b}\right) \right\} \times \left[\ln\left(\frac{V}{V^0}\right) + \sum_{j=1}^{\infty} \left(\frac{b^{-j}(V^j - (V^0)^j)}{j \times j!} \right) \right], \quad (4)$$

where $V^0(T_0) = V(P^0, T_0)$ and $V^0 = V(P^0, T)$.

The volume V^0 is related to the thermal expansivity α^0 as:

$$V^0(T) = V^0(T_0) \times \exp\left(\int_{T_0}^T \alpha^0 dT\right) \quad (5)$$

In our thermodynamic assessment of Mg_2SiO_4 , the thermal expansivity at 0.1 MPa pressure is expressed as a polynomial function of temperature.

The pressure derivative of the isothermal bulk modulus, which is an important property in geophysics, is accessible to experimentation and is derived from Eq. (3) as:

$$K' = \left(\frac{\partial K}{\partial P} \right)_T = -\frac{V}{b}. \quad (6)$$

The difference between our equation of state and those which are frequently used in geophysics and materials science, e.g. a Murnaghan or Birch–Murnaghan equation of state, is that, apart from the volume, V^0 , the pressure-volume-temperature relation of a substance is described with only two substance-dependent parameters, b and $K^0(T_0)$. This is particularly useful when experimental data for a substance are lacking.

The Gibbs energy

The molar Gibbs energy of a form of a substance at arbitrary pressure and temperature conditions is written as:

$$G_m(T, P) = \Delta H_{f,m}^0 + \int_{T_0}^T C_{P,m}^0 dT - T \cdot \left\{ S_m^0 + \int_{T_0}^T \frac{C_{P,m}^0}{T} dT \right\} + \int_{P^0}^P V_m dP, \quad (7)$$

where T denotes thermodynamic temperature, P pressure, $\Delta H_{f,m}^0$ the heat of formation, S_m^0 the absolute entropy both at reference temperature T_0 and reference pressure P^0 . The molar heat capacity at 0.1 MPa pressure is expressed as a polynomial function of temperature.

With the equation of state, Eq. (4), and dropping the subscript m , the last term of Eq. (7) becomes:

$$\int_{P^0}^P V dP = \int_{P^0, V^0}^{P, V} d(PV) - \int_{V^0}^V P dV = V(P - P^0) + K^0(T_0) \left\{ \exp\left(-\frac{V^0(T_0)}{b}\right) \right\} \times \left\{ V * \ln\left(\frac{V}{V^0}\right) - (V - V^0) + \sum_{j=1}^{\infty} \left[\frac{b^{-j}}{j \times j!} \times \left(\frac{V^{j+1} - (V^0)^{j+1}}{j+1} - (V^0)^j (V - V^0) \right) \right] \right\}, \quad (8)$$

where $V^0(T_0) = V(P^0, T_0)$ and $V^0 = V(P^0, T)$.

From the Gibbs energy all thermodynamic properties can be derived as a function of temperature and pressure.

Selection of experimental data at 0.1 MPa pressure

In Table 1, we give a summary of the data we used in our investigation.

The enthalpy of formation and the absolute entropy at $P = 0.1$ MPa pressure and $T = 298.15$ K is available only for α - Mg_2SiO_4 in the compilations of Barin (1989) and Chase et al. (1985). The heat capacity in these compilations is based on the measurements of Kelley (1943) in the temperature range 53–295 K and the drop calorimetry measurements of Orr (1953) in the temperature range 298.15–1808 K. The thermal expansivity measurements on this polymorph of Suzuki (1975) were carried out on an olivine single-crystal sample containing 92.3 mol% Mg_2SiO_4 (forsterite) component. In 1983, Suzuki et al. reported the first thermal expansivity measurements on a pure sample of α - Mg_2SiO_4 .

Results at 0.1 MPa pressure

We started the thermodynamic assessment with direct polynomial fits of the experimental heat-capacity data of the three polymorphs. The obtained expressions were constrained in a later stage of the investigation by the optimisation of all available experimental data, such as volume, thermal expansivity and adiabatic bulk modulus, as a function of pressure and temperature, and phase-boundary data. The final result of the thermo-

dynamic assessment of the three polymorphs of Mg_2SiO_4 is given in Tables 2 and 3.

To reach better agreement with the data above room temperature, we directed the optimisation of the heat capacity of α - Mg_2SiO_4 towards the high-temperature measurements of Orr (1953) and Gillet et al. (1991). As a consequence, the deviation of our result from the accurate adiabatic calorimetry data of Robie (1982) becomes more than 1% at temperatures lower than 160 K. Therefore, we restrict our thermodynamic description of the system to temperatures higher than 200 K. Because experimental data for α - Mg_2SiO_4 are available up to almost the melting point, we kept the obtained heat-capacity expression fixed in all further optimisations of the system. A reproduction of the experimental data is shown in Fig. 1 and Table 4. The enthalpy of formation and the absolute entropy, shown in Table 3, of this polymorph are taken from Barin (1989) and Chase et al. (1985).

For β - Mg_2SiO_4 and γ - Mg_2SiO_4 we directed the optimisation towards the heat capacity data of Ashida et al. (1987) which cover a larger temperature range than those of Watanabe (1982). Starting from direct fits, the expressions for the heat capacity were modified slightly (by less than 2% at 2000 K and less than 0.5% in the experimental temperature range) by the simultaneous optimisation of phase boundary, adiabatic bulk modulus and volume data. These results are compared with experimental data in Figs. 2 and 3 and Table 4.

Table 1 Summary of experimental data at 0.1 MPa pressure used in this investigation. The abbreviation *DSC* stands for differential scanning calorimetry and RPR for rectangular parallelepiped resonance. α denotes the olivine, β the wadsleyite and γ the ringwoodite form of Mg_2SiO_4

Form	Property	Temperature range in K	Technique	Reference	
α	C_P	5–380	Adiabatic calorimetry	Robie et al. (1982)	
		350–700	DSC	Watanabe (1982)	
		298–2171	Compilation	Barin (1989)	
		100–2171	Compilation	Chase et al. (1985)	
		180–700	DSC	Ashida et al. (1987)	
	α	Drop calorimetry	780–1850	Drop calorimetry	Gillet et al. (1991)
			300–1273	Dilatometry	Suzuki (1975)
		Dilatometry	300–1223	Dilatometry	Suzuki (1984); Suzuki et al. (1983)
			280–1020	Fizeau interferometry	Matsui and Manghnani (1985)
			300–1200	Dilatometry	White et al. (1985)
		K_S	300–1200	Dilatometry	Kajiyoshi (1986)
				Raman spectroscopy	Gillet et al. (1991)
			400–2160	Synchrotron radiation	Bouhifd et al. (1996)
			83–673	RPR	Sumino et al. (1977)
			100–1200	RPR	Matsui and Manghnani (1985)
β	C_P	350–700	DSC	Watanabe (1982)	
		180–700	DSC	Ashida et al. (1987)	
	K_S	293–1073	X-ray powder diffraction	Suzuki (1980)	
		300	Brillouin spectroscopy	Sawamoto et al. (1984)	
		300	Brillouin spectroscopy	Weidner et al. (1984)	
γ	C_P	350–700	DSC	Watanabe (1982)	
		180–700	DSC	Ashida et al. (1987)	
	K_S	293–1073	X-ray powder diffraction	Suzuki (1979)	
		300	Brillouin spectroscopy	Weidner et al. (1984)	
		298–873	Brillouin spectroscopy	Jackson et al. (2000)	

Table 2 Thermodynamic properties at 0.1 MPa of the three polymorphs of Mg_2SiO_4 . The heat capacity C_P (expressed in $\text{J K}^{-1} \text{mol}^{-1}$) and thermal expansivity α (expressed in K^{-1}) are

Property	Form	c_1	c_2	c_3	c_4	c_5
C_P	α	175.6606	1.5800×10^{-2}	-1.5738×10^4	-1.1924×10^6	1.3171×10^8
	β^a	176.4738	1.5590×10^{-2}	-1.9564×10^4		
	γ^a	186.8197	4.5884×10^{-3}	-2.4822×10^4	5.7363×10^5	
	β^b	171.8413	2.1600×10^{-2}	-1.8800×10^4		
	γ^b	193.9195	4.3333×10^{-3}	-2.9475×10^4	1.2479×10^6	
	α	α^a	2.2857×10^{-5}	1.2515×10^{-8}	4.2548×10^{-3}	-1.5406
	α^b	2.8320×10^{-5}	7.5800×10^{-9}			
	β	3.2820×10^{-5}	4.3355×10^{-9}	-2.7233×10^{-3}	-0.4148	35.7244
	γ	2.5684×10^{-5}	3.3538×10^{-9}	-2.4109×10^{-4}	-0.8205	58.5420

^a Optimisation based on the thermal expansivity of Kajiyoshi (1986)

^b Optimisation based on the thermal expansivity of Bouhifd et al. (1996)

Table 3 Thermodynamic properties at 298.15 K and 0.1 MPa pressure. The heat of formation is expressed in J mol^{-1} , the absolute entropy in $\text{J K}^{-1} \text{mol}^{-1}$, the molar volume in $\text{cm}^3 \text{mol}^{-1}$, the isothermal and adiabatic bulk modulus in GPa, the pressure deri-

vative of the isothermal bulk modulus being dimensionless. The unit of the equation of state constant a is $\text{m}^3 \text{K}^{-1} \text{mol}^{-1}$. α denotes the olivine, β the wadsleyite and γ the ringwoodite form of Mg_2SiO_4

Form	ΔH_f^0	S^0	V^0	$K^0(T_0)$	$a \times 10^{10}$	$K'_0(T_0)$	$K''_0(T_0)$
α^a	-2176935	95.139	43.67	127.43 ± 0.50	-2.691 ± 0.036	4.60 ± 0.02	128.75
α^b	-2176935	95.139	43.67	127.43 ± 0.50	-2.217 ± 0.036	4.60 ± 0.02	128.75
β^a	-2147081	92.247	40.54	170.26 ± 2.00	0.000	4.21 ± 0.05	171.70
β^b	-2147660	92.067	40.54	170.26 ± 2.00	0.000	4.21 ± 0.05	171.70
γ^a	-2135732	89.856	39.65	181.02 ± 3.00	-2.759 ± 0.090	4.40 ± 0.15	182.26
γ^b	-2136464	89.328	39.65	181.02 ± 3.00	-2.759 ± 0.090	4.40 ± 0.15	182.27

^a Optimisation based on the thermal expansivity of Kajiyoshi (1986)

^b Optimisation based on the thermal expansivity of Bouhifd et al. (1996)

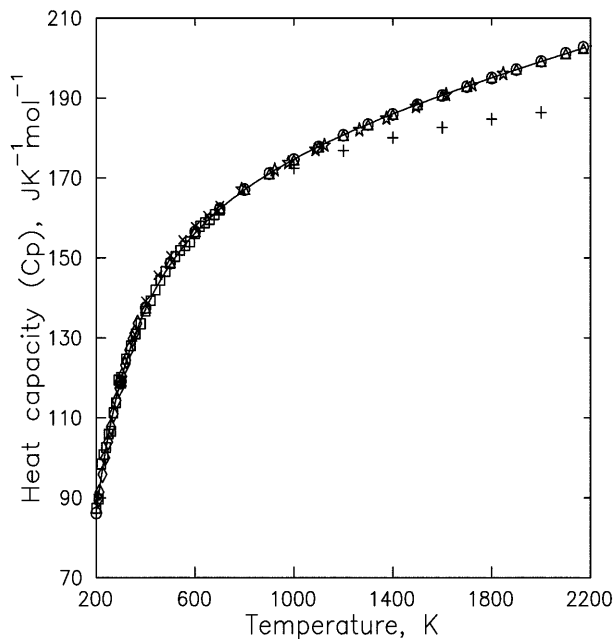


Fig. 1 Heat capacity (C_P) of $\alpha\text{-Mg}_2\text{SiO}_4$ at 0.1 MPa pressure together with experimental datapoints of \diamond Robie (1982); \times Watanabe (1982); \circ Chase et al. (1985); \square Ashida et al. (1987); $+$ Ashida et al. (1987) extrapolated using a vibrational model; \triangle Barin (1989); \star Gillet et al. (1991)

In the thermodynamic description of $\alpha\text{-Mg}_2\text{SiO}_4$ we arrived at the difficulty that there is a considerable disagreement in the thermal expansivity data, see Fig. 4. We therefore considered two thermodynamic assessments of the system; one adopting the thermal expansivity data of Kajiyoshi (1986), frequently used in earlier investigations, and one adopting the more recent data of Bouhifd et al. (1996).

To derive the constants $K^0(T_0)$ and b , in our equation of state (4), we used the relation between the adiabatic bulk modulus K_S and isothermal bulk modulus K ,

$$K = K_S \cdot \frac{C_V}{C_P}, \quad (9)$$

where C_V is the heat capacity at constant volume, and the relation

$$C_P - C_V = \alpha^2 \cdot K \cdot V \cdot T, \quad (10)$$

to find the isothermal bulk modulus as a function of temperature at 0.1 MPa pressure

$$K = \frac{C_P \cdot K_S}{C_P + \alpha^2 \cdot K_S \cdot V \cdot T}. \quad (11)$$

Using the adopted value for the molar volume given by Jeanloz and Thompson (1983), the linear relationship between volume and the logarithm of the isothermal bulk modulus, Eq. (1), together with Eq. (5), the values

Table 4 Summary of the reproduction of the heat capacity and adiabatic bulk modulus data at 0.1 MPa pressure for the three polymorphs of Mg_2SiO_4 . The thermal expansivity of $\alpha\text{-Mg}_2\text{SiO}_4$ is taken from Kajiyoshi (1986)

Property	Maximum absolute deviation (%)	Average absolute deviation (%)	Temperature range (K)	Reference
Heat capacity $\alpha\text{-Mg}_2\text{SiO}_4$	0.36	0.09	300–2171	Barin (1989)
	0.51	0.14	780–1850	Gillet et al. (1991)
	1.42	0.18	200–2171	Chase et al. (1985)
	3.24	0.67	170–700	Ashida et al. (1987)
	1.46	0.78	200–380	Robie et al. (1982)
Heat capacity $\beta\text{-Mg}_2\text{SiO}_4$	4.00	0.97	180–700	Ashida et al. (1987)
	1.25	0.54	350–750	Watanabe (1982)
Heat capacity $\gamma\text{-Mg}_2\text{SiO}_4$	4.35	1.00	180–170	Ashida et al. (1987)
	3.69	1.91	350–700	Watanabe (1982)
Thermal expansivity $\beta\text{-Mg}_2\text{SiO}_4$	0.97	0.49	273–1200	Suzuki (1980)
Thermal expansivity $\gamma\text{-Mg}_2\text{SiO}_4$	0.30	0.14	273–1200	Suzuki (1979)
Adiabatic bulk modulus $\alpha\text{-Mg}_2\text{SiO}_4$	0.10	0.06	300–1700	Isaak et al. (1989)
	1.32	0.43	300–1213	Suzuki et al. (1983)
	0.41	0.30	200–1200	Matsui and Manghnani (1985)
Adiabatic bulk modulus	0.82	0.54	200–1700	Sumino et al. (1977)
	1.34	1.34	300	Sawamoto et al. (1984)
	1.34	1.34	300	Weidner et al. (1984)
Adiabatic bulk modulus $\beta\text{-Mg}_2\text{SiO}_4$	0.23	0.11	573–873	Li et al. (1988)
	2.02	0.97	298–873	Jackson et al. (2000)
Adiabatic bulk modulus $\gamma\text{-Mg}_2\text{SiO}_4$				

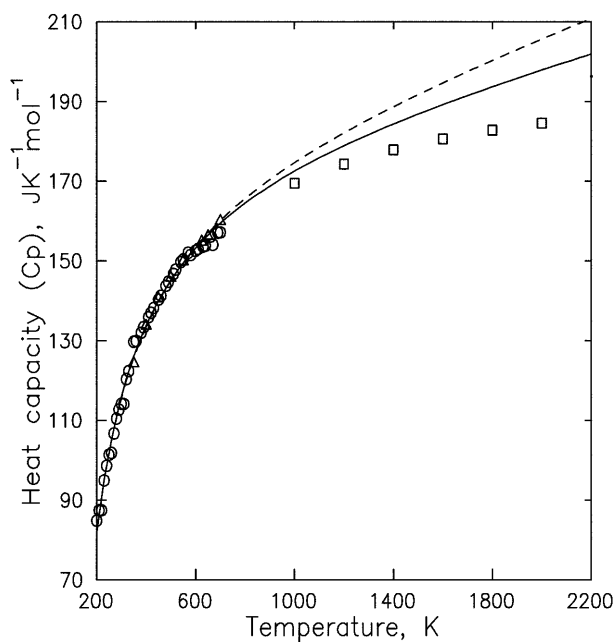


Fig. 2 Heat capacity (C_p) of $\beta\text{-Mg}_2\text{SiO}_4$ at 0.1 MPa pressure together with experimental data of Δ Watanabe (1982); \circ Ashida et al. (1987); \square Ashida et al. (1987) extrapolated using a vibrational model. *Solid curve* Optimisation using thermal expansivity of $\alpha\text{-Mg}_2\text{SiO}_4$ from Kajiyoshi (1986); *dashed curve* optimisation using thermal expansivity of $\alpha\text{-Mg}_2\text{SiO}_4$ from Bouhifd et al. (1996)

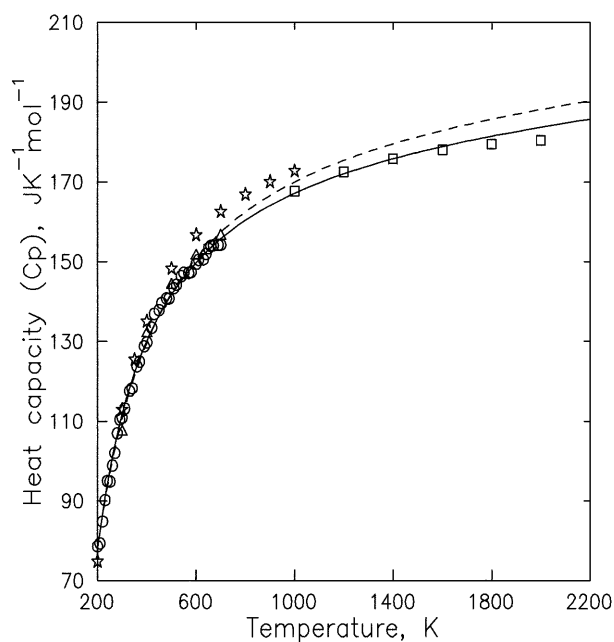


Fig. 3 Heat capacity (C_p) of $\gamma\text{-Mg}_2\text{SiO}_4$ at 0.1 MPa pressure together with experimental data of Δ Watanabe (1982); \circ Ashida et al. (1987); \square Ashida et al. (1987) extrapolated using a vibrational model; \star Chopelas et al. (1994) using a vibrational model. *Solid curve* Optimisation using thermal expansivity of $\alpha\text{-Mg}_2\text{SiO}_4$ from Kajiyoshi (1986); *dashed curve* optimisation using thermal expansivity of $\alpha\text{-Mg}_2\text{SiO}_4$ from Bouhifd et al. (1996)

for $K^0(T_0)$ and b are easily found. The value of b is inserted in Eq. (6) to determine the value of $K'_0(T_0)$. We directed the optimisation towards the most recent adiabatic bulk modulus data of Isaak et al. (1989) using the

expression for the heat capacity (C_p) given in Table 2. The average absolute deviation of our result with the data of Isaak et al. (1989) is less than 0.5% and within their experimental error limits. The resulting value for

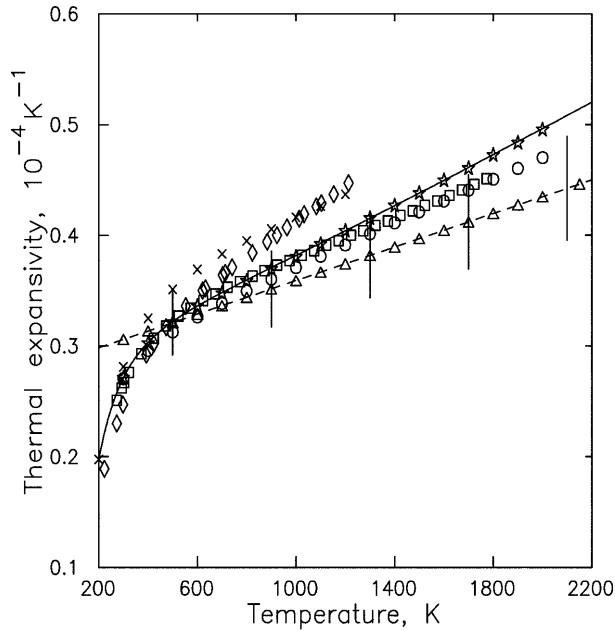


Fig. 4 Thermal expansivity of α - Mg_2SiO_4 at 0.1 MPa pressure together with experimental data of \square Suzuki (1975); \diamond Suzuki et al. (1984); \times Matsui and Manghnani (1985); \star Kajiyoshi (1986); \circ Gillet et al. (1991); \triangle Bouhifd et al. (1996) including error bars. The dashed curve represents the optimised result of Bouhifd et al. (1996). Datapoints above $T = 1200$ K are extrapolated

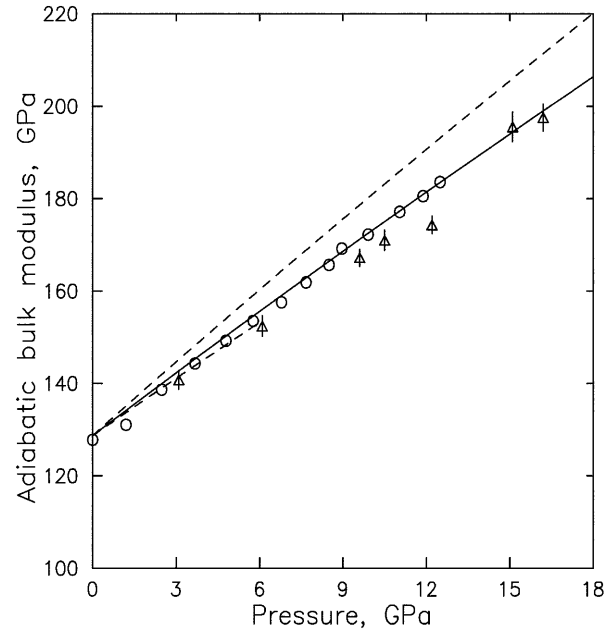


Fig. 5 Adiabatic bulk modulus of α - Mg_2SiO_4 as a function of pressure at 300 K together with experimental data of \triangle Duffy et al. (1995) and Zha et al. (1996); \circ Li et al. (1996). The lower dashed curve represents the experimental result of Yoneda and Morioka (1992). The upper dashed curve represents the predicted curve based on the $(\partial K_s/\partial P)_{T=300} = 5.37$ from Kumazawa and Anderson (1969)

$K'_0(T_0)$ is 5.38 ± 0.02 , which is identical to that given by Kumazawa and Anderson (1969), between 5.33 and 5.39. However, more recent investigations of Yoneda and Morioka (1992), Duffy et al. (1995), Zha et al. (1996) and Li et al. (1996) indicate that the value of $K'_0(T_0)$ should be smaller, between 4.2 and 4.5. The measurements of these investigators cover a larger pressure range compared to those of Kumazawa and Anderson (1969). The difference between the datasets is depicted in Fig. 5. The smaller value for $K'_0(T_0)$ has as consequence that the experimental adiabatic bulk modulus data of Isaak et al. (1989) cannot be described accurately with the use of the constants $K^0(T_0)$ and b . This can be explained in more detail as follows. From basic thermodynamics, the identity

$$\left(\frac{\partial K}{\partial T}\right)_V = \left(\frac{\partial K}{\partial T}\right)_P + \alpha K \left(\frac{\partial K}{\partial P}\right)_T, \quad (12)$$

is established, see Anderson (1995). From the linear relationship written in the form of Eq. (3), it follows that $(\partial K/\partial T)_P = \alpha K V$. Combination of the latter identity with Eq. (6) for $(\partial K/\partial T)_P$ and Eq. (12) leads to $(\partial K/\partial T)_V = 0$, a general characteristic when applying our equation of state. Because we can describe the adiabatic bulk modulus data of Isaak et al. (1989) within experimental error limits, when using $(\partial K/\partial T)_P = 5.38$ established by Kumazawa and Anderson (1969), the derivative $(\partial K/\partial T)_V$ is apparently zero. Changing $(\partial K/\partial T)_P$ to a lower value inevitably leads to a negative value for $(\partial K/\partial T)_V$.

To incorporate the recent adiabatic bulk modulus data, given in Fig. 5, we introduced a temperature dependence of the equation of state constants to take non-zero values of $(\partial K/\partial T)_V$ into account. In one session of calculations we used a linear temperature dependence of the parameter b in Eq. (1) and in another session we wrote the linear relationship as:

$$V_m(T, P) = V_m^0(T_0) + a \cdot (T - T_0) + b \cdot \ln\left(\frac{K(T, P)}{K^0(T_0)}\right). \quad (13)$$

Both sessions of calculations lead to equivalent values of thermochemical and thermophysical properties and the derivatives $(\partial K/\partial T)_P$, $(\partial K/\partial T)_V$ and $(\partial K/\partial P)_T$ in the pressure range between 0.1 MPa–30 GPa and temperature range 200–2000 K. Although the choice of the temperature dependence in the linear relationship is arbitrary, mathematical expressions for the derivatives $(\partial K/\partial T)_P$ and $(\partial K/\partial T)_V$ resulting from Eq. (13) are simpler, for example the latter is expressed as:

$$\left(\frac{\partial K}{\partial T}\right)_V = -\frac{a \cdot K}{b}. \quad (14)$$

We therefore report the optimisation of the datasets at 0.1 MPa pressure and those at high pressures with the three parameters a , b and $K^0(T_0)$ in Eq. (13) using the thermal expansivity at 0.1 MPa pressure of Kajiyoshi (1986) or Bouhifd et al. (1996). The introduction of the constant a has the consequence that in Eqs. (3), (4) and

(8), the term $K^0(T_0) \cdot \exp[-V^0(T)/b]$ is replaced by the term $K^0(T_0) \cdot \exp[-V^0(T)/b] \cdot \exp[a \cdot (T_0 - T)/b]$.

We find a value for $a = (-2.691 \pm 0.036) \times 10^{-10} \text{ m}^3 \text{ K}^{-1} \text{ mol}^{-1}$ and $a = (-2.217 \pm 0.036) \times 10^{-10} \text{ m}^3 \text{ K}^{-1} \text{ mol}^{-1}$ when using the thermal expansivities of Kajiyoshi (1986) and Bouhifd et al. (1996), respectively. Applying Eq. (14), the average value of $(\partial K/\partial T)_V$ in the temperature range between 300 and 2000 K and 0.1 MPa pressure is $-0.003 \text{ GPa K}^{-1}$, which is about 14% of the average value of $(\partial K/\partial T)_P$. The reproduction of the adiabatic bulk modulus at 0.1 MPa pressure is shown in Fig. 6 and Table 4.

It can be shown from Eq. (13) that a negative value for a has the consequence that the thermal expansivity will become negative at high pressures, resulting in a loss of physical realism. Using the calculated value for a , the thermal expansivity becomes negative at 114 GPa and 300 K. For temperatures above 700 K, it becomes negative for pressures higher than 140 GPa. To investigate if the anomaly could be removed by the use of a Murnaghan or a third-order Birch-Murnaghan equation of state, we fitted our result of the isothermal compressibility of $\alpha\text{-Mg}_2\text{SiO}_4$ with a four-parameter polynomial (see Table 5). For a Murnaghan equation of state we find that the thermal expansivity becomes negative at $(T/\text{K}, P/\text{GPa}) = (300, 93), (1000, 146), (2000, 111)$, respectively. For a third-order Birch-Murnaghan equation of state we find $(300, 66), (1000, 76)$ and $(2000, 62)$, respectively. The

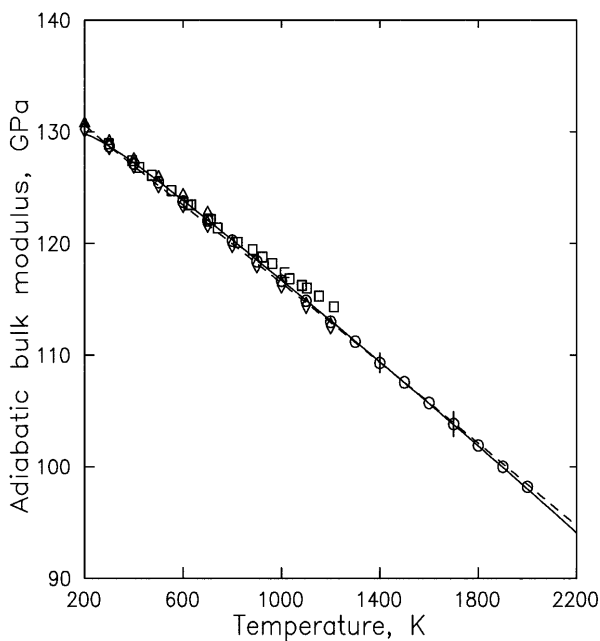


Fig. 6 Adiabatic bulk modulus of $\alpha\text{-Mg}_2\text{SiO}_4$ at 0.1 MPa pressure together with experimental data of \triangle Sumino et al. (1977); \diamond Matsui and Manghni (1985); \square Suzuki et al. (1983); \circ Isaak et al. (1989) including error bars at 1400 and 1700 K. Data above $T = 1700 \text{ K}$ are extrapolated. *Solid curve* Optimisation using thermal expansivity of $\alpha\text{-Mg}_2\text{SiO}_4$ from Kajiyoshi (1986); *dashed curve* optimisation using thermal expansivity of $\alpha\text{-Mg}_2\text{SiO}_4$ from Bouhifd et al. (1996)

anomaly is thus not removed but is present at pressures far outside the region of the experimental investigations.

In Fig. 7 we have plotted the calculated heat capacity at constant volume, C_V , at 0.1 MPa pressure using the input values given in Tables 2 and 3 together with data obtained from theoretical studies. From Fig. 7 it is clear that from C_V it is not possible to make a decision which favours a certain course of the thermal expansivity. From the C_V calculations of Cynn et al. (1996), we conclude that the thermal expansivity must resemble that obtained by Kajiyoshi (1986). On the other hand, the C_V calculations of Gillet et al. (1991) indicate that the thermal expansivity should be lower than those measured by Kajiyoshi (1986).

Table 5 Calculated isothermal compressibility (in Pa^{-1}), $\kappa = k_1 + k_2 \times T + k_3 \times T^2 + k_4 \times T^3$ at 0.1 MPa pressure. The results are obtained by fitting the calculated isothermal compressibility in the temperature range 200–2000 K, resulting from Eqs. (3) and (13) together with the values given in Table 3. For $\alpha\text{-Mg}_2\text{SiO}_4$, the thermal expansivity of Kajiyoshi (1986) has been taken

Modification of Mg_2SiO_4	$k_1 \times 10^{12}$ (Pa^{-1})	$k_2 \times 10^{16}$ ($\text{Pa}^{-1} \text{ K}^{-1}$)	$k_3 \times 10^{19}$ ($\text{Pa}^{-1} \text{ K}^{-2}$)	$k_4 \times 10^{23}$ ($\text{Pa}^{-1} \text{ K}^{-3}$)
α	7.4976	10.8593	2.8701	6.7050
β	5.7022	4.8489	2.4274	-1.0967
γ	5.3255	5.9733	1.8602	-0.5931

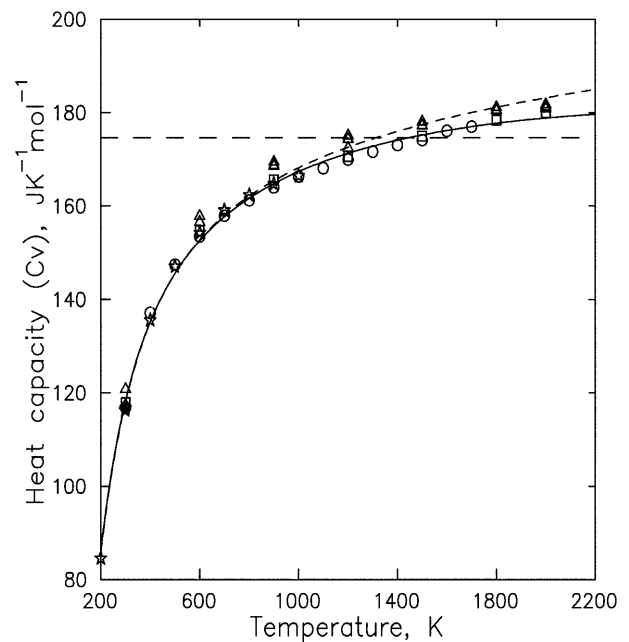


Fig. 7 Heat capacity (C_V) of $\alpha\text{-Mg}_2\text{SiO}_4$ at 0.1 MPa pressure together with theoretical data of \star Chopelas (1990); \triangle Gillet et al. (1991) using different anharmonic models; \circ Cynn et al. (1996); \square Gillet et al. (1991) by combining their measured C_P together with bulk moduli of Isaak et al. (1989) and thermal expansivity data of Kajiyoshi (1986). *Solid curve* Optimisation using thermal expansivity of $\alpha\text{-Mg}_2\text{SiO}_4$ from Kajiyoshi (1986). *Horizontal dashed line* Dulong-Petit limit; *upper dashed curve* optimisation using thermal expansivity data of Bouhifd et al. (1996)

A thermodynamic assessment of the systems Fe–Mg–O and Fe–Mg–Si–O has been carried out by Fabrichnaya (1998) resulting in thermal expansivity descriptions for the β and γ forms of Mg_2SiO_4 which deviate substantially from the reported error limits in experiments. In our optimisation of the thermal expansivity of $\beta\text{-Mg}_2\text{SiO}_4$ and $\gamma\text{-Mg}_2\text{SiO}_4$ we have adopted the experimental data of Suzuki (1979, 1980). Using Grüneisen's theory of thermal expansivity, Suzuki extrapolated the experimental data above 1200 K up to 2200 K. We have included these extrapolations in our optimisation. Our results for these two polymorphs are compared with Suzuki's data in Fig. 8 and Table 4. The data are reproduced far within the reported experimental error limits.

For $\beta\text{-Mg}_2\text{SiO}_4$ we have directed our optimisation of the adiabatic bulk modulus towards the recent data of Li et al. (1998) to find the constants $K^0(T_0)$ and b . Optimisation of their data in the temperature region of 573 to 873 K leads to an adiabatic bulk modulus of (171.7 ± 2.0) GPa and a pressure derivative $(\partial K_S/\partial P)_T = 4.21 \pm 0.05$ at 298 K and 0.1 MPa pressure. These values match the experimental values (172 ± 2) GPa and 4.2 ± 0.1 , respectively. The calculated adiabatic bulk modulus is also in agreement with the experimental value of (174 ± 6) GPa from Weidner et al. (1984). The pressure derivative $(\partial K_S/\partial P)_T$ deviates from the experimental value, 4.8, of Gwanmesia et al. (1990). From the analysis it follows that the constant $a = 0$ and with Eq. (14), it follows that $(\partial K/\partial T)_V = 0$.

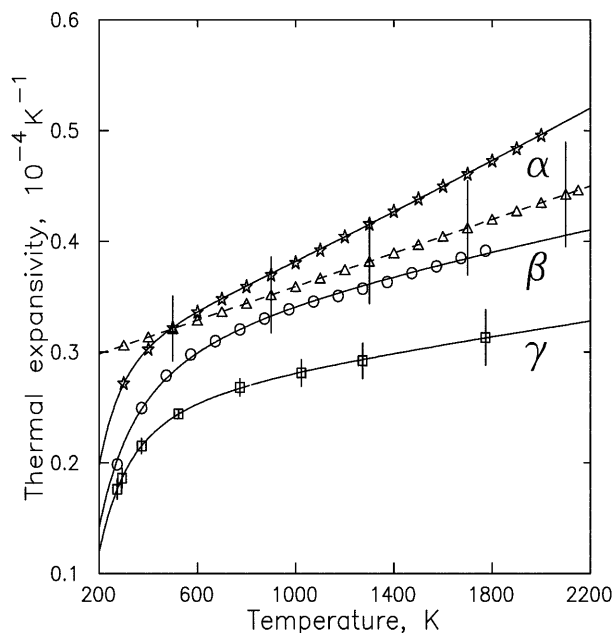


Fig. 8 Thermal expansivity of the three polymorphs of Mg_2SiO_4 at 0.1 MPa pressure together with experimental data of: Mg_2SiO_4 (α): \star Kajiyoshi (1986); \triangle Bouhifd et al. (1996) including error bars; Mg_2SiO_4 (β): \circ Suzuki (1980); Mg_2SiO_4 (γ): \square Suzuki (1979) including error bars. *Dashed curve* represents the optimised result of Bouhifd et al. (1996)

For $\gamma\text{-Mg}_2\text{SiO}_4$ we used the recent adiabatic bulk modulus measurements of Jackson et al. (2000) in the temperature range of 298–873 K in combination with the volume measurements of Meng et al. (1993, 1994). The optimisation leads to an adiabatic bulk modulus of (182.3 ± 3.0) GPa at ambient conditions, which is in good agreement with the value of (184 ± 3) GPa of Weidner et al. (1984) and the value (185 ± 3) GPa of Jackson et al. (2000). The calculated pressure derivative $(\partial K/\partial P)_T = 4.4 \pm 0.15$ at ambient conditions reproduces the value 4.2 ± 0.3 determined by Meng et al. (1994) but deviates from the value, 5.0, given by Rigden et al. (1991). Applying Eq. (14), the average value of $(\partial K/\partial T)_V$ in the temperature range between 300–2000 K and 0.1 MPa pressure is -0.005 GPa/K which is about 21% of the average value of $(\partial K/\partial T)_P$.

The adiabatic bulk modulus data of $\beta\text{-Mg}_2\text{SiO}_4$ and $\gamma\text{-Mg}_2\text{SiO}_4$ are compared with the experimental data in Fig. 9 and Table 4.

Results at high pressure

Single-crystal compressibility of $\alpha\text{-Mg}_2\text{SiO}_4$ has been measured by Kudoh and Takéuchi (1985), Andraut et al. (1995), Downs et al. (1996) and by Zhang (1998). Andraut et al. (1995) used powder diffraction with synchrotron radiation whereas the other investigators

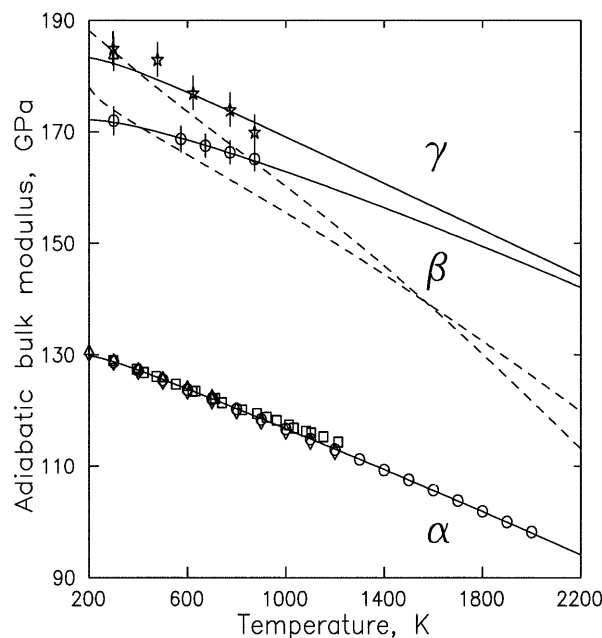


Fig. 9 Adiabatic bulk modulus of the three polymorphs of Mg_2SiO_4 at 0.1 MPa pressure together with experimental data of: $\alpha\text{-Mg}_2\text{SiO}_4$: \triangle Sumino et al. (1977); \diamond Matsui and Manghnani (1985); \square Suzuki et al. (1983); \circ Isaak et al. (1989) with extrapolation above $T = 1700$ K; $\beta\text{-Mg}_2\text{SiO}_4$: \circ Li et al. (1998) including error bars; $\gamma\text{-Mg}_2\text{SiO}_4$: \triangle Weidner et al. (1984) including error bar; \star Jackson et al. (2000) including error bars. *Dashed curves* represent calculations for the β and γ forms using the database of Fabrichnaya (1998)

used four-circle X-ray diffractometry. Will et al. (1986) measured the compressibility with X-ray diffractometry using energy-dispersive techniques on polycrystalline synthetic α -Mg₂SiO₄. In all experiments, performed at room temperature and up to 23 GPa, no phase transition from the α -Mg₂SiO₄ form to the β -Mg₂SiO₄ or γ -Mg₂SiO₄ form was detected. Andrault et al. (1995) found that α -Mg₂SiO₄ undergoes a transformation to amorphous material at pressures higher than 40 GPa and room temperature. In the derivation of the equation of state parameters a , b and $K^0(T_0)$ for α -Mg₂SiO₄ we directed the optimisation towards the recent adiabatic bulk modulus data of Li et al. (1996), resulting in a satisfactory reproduction of experimental volume data, see Table 6. In Fig. 10 we have plotted the volume as a function of pressure at room temperature together with the experimental data. The reproduction of the adiabatic bulk modulus data is given in Table 6 and plotted in Fig. 5.

The compressibility of β -Mg₂SiO₄ has been measured by Mizukami et al. (1975) using a multianvil high-pressure X-ray apparatus. More recently, the compressibility has been measured by Meng et al. (1993) using synchrotron X-ray radiation in a cubic anvil cell apparatus. Figure 10 and Table 6 show that the experimental data are reproduced to a satisfactory extent.

Mizukami et al. (1975) and Meng et al. (1993, 1994) have determined the compressibility of γ -Mg₂SiO₄. For this polymorph we find that by using the constants b and $K^0(T_0)$ we could not reproduce both the data sets of Meng et al. (1993, 1994) and the adiabatic bulk modulus measurements of Jackson et al. (2000) with the same value of $K^0(T_0)$ and b (or K'_0). Directing the optimisation towards the former investigators leads to $K'_0 = 4.5$, which is in accordance with their experimentally derived value of 4.2 ± 0.3 . The result gives rise to a good reproduction of the 300 and 700 K isotherms up

to 30 GPa to within 0.3% (mean deviation 0.14%) but the calculated adiabatic bulk modulus of Jackson et al. (2000) is poorly reproduced. The calculated value $K^0(T_0) = 175$ GPa leads to a calculated value $K'_S(T_0) = 176.3$ GPa, which is 9 GPa below their experimental value. To explain their data, Meng et al. (1994) introduced a thermal expansivity at 0.1 MPa pressure, which deviates far outside the error limits given

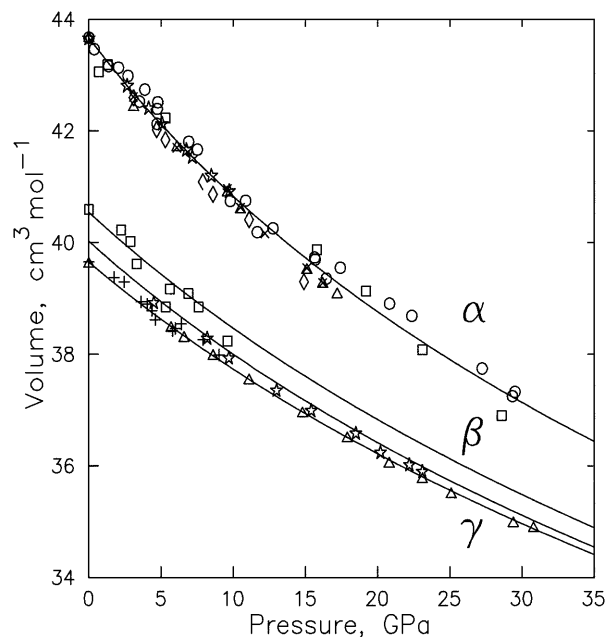


Fig. 10 Molar volumes at room temperature of the three polymorphs of Mg₂SiO₄ together with experimental data of: α -Mg₂SiO₄: \diamond Kudoh and Takéuchi (1985); \circ Will et al. (1986); \square Andrault et al. (1995); \triangle Downs et al. (1996); \times Zha et al. (1996); \star Zhang (1998); β -Mg₂SiO₄: \square Mizukami et al. (1975); γ -Mg₂SiO₄: $+$ Mizukami et al. (1975); \triangle Meng et al. (1994) at 300 K; \star Meng et al. (1994) at 700 K

Table 6 Summary of the reproduction of the volume and adiabatic bulk modulus data at high pressure for the three polymorphs of Mg₂SiO₄. The thermal expansivity of α -Mg₂SiO₄ is taken from Kajiyoshi (1986)

Property	Maximum absolute deviation (%)	Average absolute deviation (%)	Temperature range (K)	Pressure range (GPa)	Reference
Volume	1.13	0.57	300	3.1–14.9	Kudoh and Takéuchi (1985)
α -Mg ₂ SiO ₄	0.90	0.39	300	0.0–29.5	Will et al. (1986)
	0.15	0.08	1019–1371	6.6–7.6	Meng et al. (1993)
	0.86	0.51	300	0.7–23.1	Andrault et al. (1995)
	0.51	0.30	300	0.0–17.2	Downs et al. (1996)
	0.52	0.29	300	3.1–16.2	Zha et al. (1996)
	0.11	0.06	300	0.0–9.7	Zhang (1998)
	Volume	1.32	0.46	300	0.0–9.6
β -Mg ₂ SiO ₄	0.70	0.67	724–872	7.5–7.6	Meng et al. (1993)
Volume	0.46	0.22	300	0.0–9.0	Mizukami et al. (1975)
γ -Mg ₂ SiO ₄	0.32	0.22	759–1122	9.7–9.9	Meng et al. (1993)
	0.12	0.05	300	0.0–30.8	Meng et al. (1994)
	0.37	0.24	700	4.5–23.1	Meng et al. (1994)
	Adiabatic bulk modulus	1.53	0.80	300	0.0–6.0
α -Mg ₂ SiO ₄	4.60	2.04	300	3.1–16.2	Zha et al. (1996)
	2.33	0.64	300	0.0–12.5	Li et al. (1996)

by Suzuki (1979). Using this thermal expansivity expression we find a perfect match (mean deviation 0.09%) of the two isotherms with $K^0(T_0) = 180.30$ GPa and $K'_0 = 4.2$. The adiabatic bulk modulus data of Jackson et al. (2000), again, are not reproduced.

Because we cannot assign shortcomings in either technique of the investigators, we used the same procedure as for α - Mg_2SiO_4 by introducing a temperature dependence of the constants used in our equation of state.

We find a value for $a = (-2.759 \pm 0.090) \times 10^{-10} \text{ m}^3 \text{ K}^{-1} \text{ mol}^{-1}$. Using the calculated value for a , the thermal expansivity becomes negative at 114 GPa and 300 K. For temperatures above 700 K, it becomes negative for pressures higher than 140 GPa. Just as for α - Mg_2SiO_4 , the use of a Murnaghan or a Birch-Murnaghan equation of state does not remove this anomaly. Table 5 shows the fits of the isothermal compressibility of γ - Mg_2SiO_4 with a four-parameter polynomial function. For a Murnaghan equation of state, the thermal expansivity becomes negative at $(T/\text{K}, P/\text{GPa}) = (300, 78), (1000, 141), (2000, 127)$. For a third-order Birch-Murnaghan equation of state we find $(300, 65), (1000, 96)$ and $(2000, 85)$, respectively. The anomaly is present at pressures far outside the region of the experimental investigations. Using the latter two equations of state, the data at 0.1 MPa pressure and the volume-pressure data of Meng et al. (1993, 1994) are reproduced with the same accuracy as with our model. The reproduction of the adiabatic bulk modulus and volume data is shown in Figs. 9 and 10 and Table 6.

To reproduce the phase equilibrium data of the three polymorphs we used the experimental data of Katsura and Ito (1989) and the calorimetric measurements of Akaogi et al. (1984, 1989). In the detailed study using an uniaxial split-sphere apparatus in combination with microfocused X-ray diffractometry, scanning electron microscopy and electron probe microanalysis, the former investigators obtained two points on each of the two phase-boundary curves associated with the α - β and β - γ phase transitions. For the α - β transition, they found these points as $(T/\text{K}, P/\text{GPa}) = (1473, 14)$ and $(1873, 15)$, respectively. For the β - γ transition the result was $(T/\text{K}, P/\text{GPa}) = (1473, 19)$ and $(1873, 21)$, respectively.

Akaogi et al. (1989) determined the enthalpy difference between the γ and β forms and between the γ and α forms of Mg_2SiO_4 at 975 K and 0.1 MPa pressure using high-temperature solution calorimetry. Akaogi et al. (1984) determined the enthalpy difference between the β and α polymorphs using the same technique. In addition the entropy differences were calculated by thermodynamic assessment of the system Mg_2SiO_4 - Fe_2SiO_4 . The phase diagram and the calorimetric data are evaluated by using Eqs. (7) and (8) and putting the constraints of thermodynamic equilibrium $G^\alpha(T, P) = G^\beta(T, P)$ and $G^\beta(T, P) = G^\gamma(T, P)$.

Using the heat-capacity expressions given in Table 2, the equation of state parameters given in Table 3, we calculated the heat of formation and the absolute entropy of β - Mg_2SiO_4 and γ - Mg_2SiO_4 . Using the phase-bound-

ary data, we were able to constrain the heat capacity, at 0.1 MPa pressure, of the β and γ forms at high temperature. In the optimisation we allowed a 1-GPa variation of the phase-boundary data. The result of the enthalpy of formation and absolute entropy of the three forms is summarised in Table 3. The optimisation results in an exact reproduction of the experimental phase equilibrium points of Katsura and Ito (1989), see Fig. 11. Due to the error limits in the thermodynamic properties, the accuracy of the calculated pressures at fixed temperatures is 0.15 GPa for the α - β transitions and 0.75 GPa for the β - γ transitions. The calculated enthalpy and entropy differences are in good agreement with the experimental data of Akaogi et al. (1989) and predicted results for the entropy of Chopelas (1990, 1991) and Chopelas et al. (1994) obtained by vibrational spectroscopy, see Table 7.

From the optimisation it appeared that by keeping the transition enthalpy $\Delta H(\beta \rightarrow \gamma)$ within the error limits reported by Akaogi et al. (1989), the transition enthalpy $\Delta H(\alpha \rightarrow \beta)$ could only be varied between 27130 and 29970 J mol^{-1} , to match all available experimental data of the three polymorphs, which is half their reported error limit. By considering the error limits in the enthalpy of formation, the calculated heat capacities vary less than 0.4% in the temperature region of the experiments and less than 3% at a temperature of 2000 K.

Discussion

In the preceding sections we have calculated thermochemical and thermophysical properties and the phase

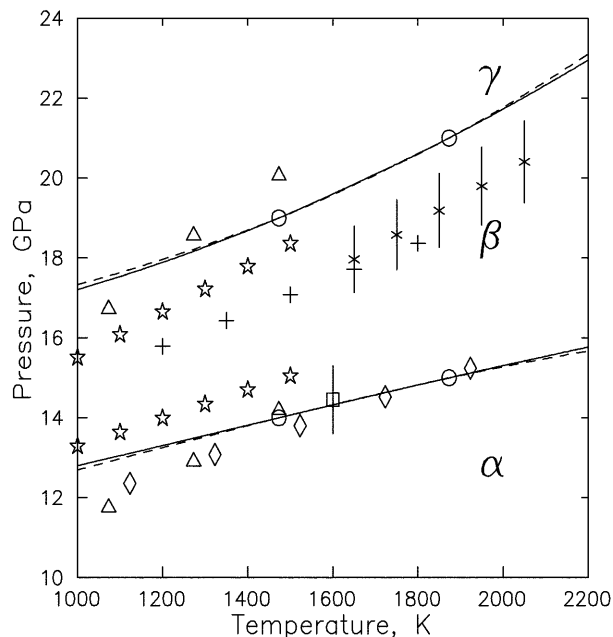


Fig. 11 Pressure-temperature phase diagram together with the experimental data of: ☆ Suito et al. (1977); + Othani (1979); × Sawamoto (1986); △ Akimoto (1987) after correction of the data of Kawada (1977); ○ Katsura and Ito (1989); □ Boehler and Chopelas (1991); ◇ Morishima et al. (1994)

Table 7 Comparison of the calculated transition enthalpies (in J mol^{-1}) and transition entropies (in $\text{J K}^{-1} \text{mol}^{-1}$) at 975 K and 0.1 MPa pressure with experimental data

Transition	ΔH	ΔS	Reference
α to β	27885 ± 1422	-6.51 ± 1.08	Calculated ^a
	27666 ± 1422	-6.33 ± 1.08	Calculated ^b
	29970 ± 2840	-7.7 ± 1.9	Akaogi et al. (1989)
		-7.34 ± 1.13	Chopelas (1990); Chopelas et al. (1994)
β to γ	8718 ± 1422	-6.90 ± 1.08	Calculated ^a
	8957 ± 1422	-6.76 ± 1.08	Calculated ^b
	9080 ± 2120	-7.3 ± 1.4	Akaogi et al. (1989)
		-7.64 ± 1.13	Chopelas (1991); Chopelas et al. (1994)
α to γ	36602 ± 1422	-13.41 ± 1.08	Calculated ^a
	36624 ± 1422	-13.09 ± 1.08	Calculated ^b
	39050 ± 2620	-15.0 ± 2.4	Akaogi et al. (1989)
		-14.98 ± 1.13	Chopelas (1990); Chopelas et al. (1994)

^aOptimisation based on the thermal expansivity of Kajiyoshi (1986)

^bOptimisation based on the thermal expansivity of Bouhifd et al. (1996)

diagram of the three polymorphs using thermal expansivity data of Kajiyoshi (1986) and Bouhifd et al. (1996) for α - Mg_2SiO_4 . Using these two datasets reveals that the values of $K^0(T_0)$ and K'_0 for the three polymorphs are identical within their experimental error limits. Changing the thermal expansivity of α - Mg_2SiO_4 influences solely the heat capacity (C_P), the heat of formation ΔH_f^0 and absolute entropy S^0 of the β - Mg_2SiO_4 and γ - Mg_2SiO_4 forms. The calorimetric data of Akaogi et al. (1984, 1989) for the enthalpy differences between the three polymorphs at 975 K and 0.1 MPa pressure are summarised in Table 7. Comparing these data with our calculations shows that differences in thermal expansivity do not correspond to enthalpy differences. Decreasing the thermal expansivity of α - Mg_2SiO_4 , into the direction of the data of Bouhifd et al. (1996), has as consequence that the entropy differences between the α and β and the α and γ forms become smaller. The calculated values are still in accordance with those obtained by Akaogi et al. (1989) and Chopelas (1990) and Chopelas et al. (1994). At the same time, the heat capacity (C_P) curves of the β and γ forms increase by 3% at 2000 K whereas they do not change in the temperature range of the experiments ($<0.5\%$).

In our assessment of the thermodynamic properties of the three polymorphs we followed an empirical approach to describe the heat capacity (C_P) and thermal expansivity at 0.1 MPa pressure with polynomial functions of temperature. Although these properties are well constrained, the number of parameters used is larger than, for instance, needed in a framework defined by the Mie-Grüneisen-Debye (MGD) formalism. This formalism, in which only six parameters are varied, has found successful application to a variety of Earth materials, as shown by Stixrude and Bukowinsky (1990) and Jackson and Rigden (1996). For α - Mg_2SiO_4 , however, the heat capacity C_V at 0.1 MPa pressure passes the Dulong-Petit limit at 1440 and 1310 K when using thermal expansivity data of Kajiyoshi (1986) and Bouhifd et al. (1996), respectively, see Fig. 7. The Debye model is therefore

not suitable, but this difficulty could be overcome with the application of more complicated models (see, e.g. Gillet et al. 1991). On the other hand, it is easily shown from the experimental data and the experimental errors therein, that the parameter q in the expression for the Grüneisen parameter in the MGD formalism, $\gamma = \gamma_0(V/V_0)^q$, must be a complicated function of temperature. The same type of reasoning also holds for β - Mg_2SiO_4 for which the experimental data constrain our empirically calculated C_P at 0.1 MPa pressure such that C_V passes the Dulong-Petit limit at 1540 and 1290 K when using the thermal expansivity data for α - Mg_2SiO_4 of Kajiyoshi (1986) and Bouhifd et al. (1996), respectively. Of the three polymorphs, only the γ form is characterised with a C_V function at 0.1 MPa pressure which approaches the Dulong-Petit limit at high temperature in our two descriptions. The MGD formalism could therefore be applied for making high-temperature extrapolations, but the 0.1 MPa experimental data clearly indicate that a more complicated expression for the Grüneisen parameter and a more complicated model for C_V are required.

Seismic discontinuities

An exploratory application of the thermodynamic analysis of the three polymorphs is the calculation of the bulk sound velocity of the three polymorphs at pressures and temperatures which prevail in the Earth. In the field of geophysics and geology, the seismic discontinuities at about 400, 520 and 650 km depth are often associated with the phase transitions between olivine (α)-wadsleyite (β), wadsleyite (β)-ringwoodite (γ) and ringwoodite (γ)-perovskite-magnesiowüstite, respectively, which could be modelled by using the ternary system MgO-FeO-SiO_2 , see Saxena (1996). The application of our analysis is exploratory because mantle rocks contain approximately 8 wt% iron, Ringwood (1991), whereas we did not consider iron in our calculations. Secondly, we did

not consider the decomposition of γ - Mg_2SiO_4 (ringwoodite) into MgSiO_3 (perovskite) and MgO (periclase), which rules out the application to the 650-km seismic discontinuity. Finally, we cannot deduce the shear wave and compressional wave velocities from our analysis without the introduction of the shear modulus as a function of pressure and temperature. From the Gibbs energy it is possible to calculate the bulk sound velocity, defined by $v = (K_S/\rho)^{1/2}$, where ρ represents density, as a function of pressure and temperature and therefore we restrict the application to this property. The Gibbs energy formulation of the three polymorphs allows the calculation of bulk sound velocities along the phase boundaries of the α , β and γ forms of Mg_2SiO_4 . By calculating bulk sound velocity profiles along isotherms through the stability fields of the three polymorphs, it appears that the difference between the sound velocities of the β and γ forms, $v^\gamma - v^\beta$, tends to decrease when the temperature increases from 900 to 2000 K whereas the velocity difference between the α and β forms, $v^\beta - v^\alpha$, increases. From these profiles we constructed bulk sound velocity differences along the α - β and β - γ phase boundaries taking the error limitations of all properties into account, as shown in Fig. 12. Inspection of this figure indicates that in the temperature range between 900 and 2000 K, the bulk sound velocity difference at the α to β phase boundary varies linearly from $(0.594 \pm 0.038) \text{ km s}^{-1}$ to $(0.675 \pm 0.038) \text{ km s}^{-1}$. The velocity contrast, a measure commonly used in tomo-

graphy, $(v^\beta - v^\alpha)/v^\alpha$ varies from $(8.37 \pm 0.53)\%$ to $(9.71 \pm 0.53)\%$. At 1300 K and 13.60 GPa, which corresponds with a depth of about 400 km in the Earth, the value of the velocity contrast is $(8.89 \pm 0.53)\%$. According to Dziewonski and Anderson (1981), the seismic velocity contrast is 4.6% at 410 km, implying that the mantle consists of 52% of Mg_2SiO_4 . Preliminary calculations of the system Mg_2SiO_4 - Fe_2SiO_4 show that the addition of iron to Mg_2SiO_4 gives rise to a 1–2% increase in the bulk sound velocity.

In the same temperature range at the β - γ transition, the bulk sound velocity difference, $v^\gamma - v^\beta$, varies from $(0.069 \pm 0.055) \text{ km s}^{-1}$ to $(-0.043 \pm 0.055) \text{ km s}^{-1}$, corresponding to a velocity contrast $(v^\gamma - v^\beta)/v^\beta$ ranging from $(0.87 \pm 0.70)\%$ to $(-0.54 \pm 0.70)\%$, respectively. The decreasing trend is caused by the fact that whereas the density difference increases from $(0.0777 \pm 0.0058) \text{ g cm}^{-3}$ to $(0.1028 \pm 0.0069) \text{ g cm}^{-3}$, the adiabatic bulk modulus difference decreases from $(9.04 \pm 3.47) \text{ GPa}$ to $(3.91 \pm 3.28) \text{ GPa}$. Figure 12 shows that changing the thermal expansivity of α - Mg_2SiO_4 from that of Kajiyoshi (1986) to that of Bouhifd et al. (1996) has virtually no effect on the calculated bulk sound velocity differences. We conclude that for a 100% Mg_2SiO_4 mantle at a temperature of about 1600 K, the bulk sound velocity jump corresponding to the 520-km seismic discontinuity in the Earth's mantle is close to zero, considering the error limitations in all experiments.

As a last step we investigated the influence of the equation of state used in our calculations. The results indicate that by fitting the isothermal compressibility at 0.1 MPa pressure resulting from our equation of state, see Table 5, the results given in Tables 2 and 3 can be used in a Murnaghan or a Birch–Murnaghan equation of state without significant loss of accuracy in the reproduction of all experimental data.

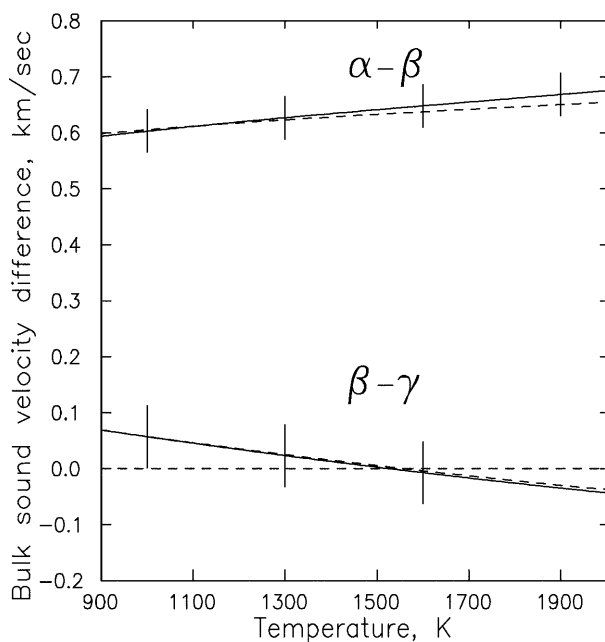


Fig. 12 Bulk sound velocity difference along the α - β and β - γ phase boundaries: *solid curves* by using the thermal expansivity data for α - Mg_2SiO_4 of Kajiyoshi (1986) and *dashed curves* by taking the thermal expansivity data of Bouhifd et al. (1996). The *vertical bars* represent the accuracy of the calculation based on the experimental error limits of the experimental data. The *horizontal dashed line* represents zero bulk sound velocity difference between two phases

Conclusions

A thermodynamic consistent Gibbs energy formulation of the polymorphs of Mg_2SiO_4 has been constructed using Grover, Getting and Kennedy's empirical relationship between volume and logarithm of the isothermal bulk modulus. Because the pressure range (0–30 GPa) is low compared with pressures prevailing in the Earth's mantle, the results can be used in combination with a Murnaghan or a Birch–Murnaghan equation of state without significant loss of accuracy in the reproduction of all experimental data. When these equations of state are used in the same manner as our equation of state, that is, expressing the isothermal bulk modulus at 0.1 MPa pressure as a polynomial function of temperature, our equation of state has the advantage that fewer parameters must be optimised. In our equation of state we optimised three parameters, $K^0(T_0)$, a and b . With a Murnaghan or Birch–Murnaghan equation of state we needed four parameters for the isothermal bulk modulus, $K^0(T)$, and additionally one parameter for its pressure

derivative, K' , at P^0 and T_0 . Compared with a Mie-Grüneisen-Debye (MGD) formalism, our empirical approach results in a description with more parameters due to polynomial functions used for the heat capacity and thermal expansivity at 0.1 MPa pressure. It can be shown, however, that the MGD formalism requires a more complicated description for the Grüneisen parameter and a more complicated model for the heat capacity at constant volume to accurately describe the complete set of experimental data.

Because considerable disagreement exists for the experimental thermal expansivity data of the α form, the influence of this property on the thermodynamic properties of the three polymorphs has been investigated. Changing the thermal expansivity of the α form of Mg_2SiO_4 from the data of Kajiyoshi (1986) to the more recent data of Bouhifd et al. (1996) increases the heat capacities of the β and γ forms at temperatures higher than 700 K, whereas the entropy differences between the β and α forms and the γ and α forms decrease. All other properties, like the pressure derivative of the bulk modulus, do not change significantly.

Our assessment of the thermodynamic properties of Mg_2SiO_4 reveals that for the α and γ forms an extra temperature dependence in the linear relationship is needed to account for non-zero values of $(\partial K/\partial T)_V$.

The bulk sound velocity contrast between the β and α forms is about 9% at pressures prevailing at 400 km depth in the Earth. The bulk sound velocity contrast between the β and γ forms is close to zero at temperatures and pressures corresponding to the 520-km seismic discontinuity in the Earth's mantle.

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