Thermoelastic properties of MgSiO₃ perovskite using the Debye approach

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Abstract

MgSiO₃ perovskite is shown to be a Debye-like mineral by the determination of specific heat, Cᵥ, entropy, S, and thermal pressure, ΔPₚₑ, using the Debye theory up to 1800 K. Sound velocities and bulk moduli at ambient conditions published by Yeganeh-Haeri were used to find the ambient acoustic Debye temperature, Θₒ. The variation of Θₒ with T was assumed to be a curve parallel to the Θₒ vs. T curves previously found for Al₂O₃, MgO, and MgSiO₃, enabling Θₒ(T) to be given up to 1800 K. To determine Cᵥ, the thermal expansivity, α, and the isothermal bulk modulus, Kᵣ, are needed. After considering several sets of α(T), the α(T) data of Funamori and his colleagues were chosen. Using the ambient Kᵣ and the values of (αKᵣ/αT) vs. T reported by Jackson and Rigden, Kᵣ(T) up to 1800 K was found. Then Cᵥ(T) up to 1800 K was found assuming quasiharmonicity in Cᵥ. The data behind the Cᵥ(T) calculation are also sufficient to find the Grüneisen parameter, γ(T), and the Anderson-Grüneisen parameters, δₛ and δ₉, up to 1800 K. The value of q = (δ ln γ/δ ln V)ₚₑ was found, and with γ and p, ΔPₑ vs. V and T was determined. The three sound velocities, vₙ, vₛ, and vₐ = √Kᵣ/p, were then determined to 1800 K. From vₙ and vₛ, Poisson's ratio and the isotropic shear modulus, G, were found to 1800 K. MgSiO₃ perovskite is one of a small, select group of Debye-like minerals for which thermoelastic properties and the equation of state (EOS) are calculable from acoustic data.

Introductory Remarks on Debye Theory

Thermoelastic properties for a Debye solid, such as Cᵥ vs. T, at P = 0 can be easily calculated from standard Debye tables. A Debye solid is a monatomic solid (typically a metal) in which thermoelastic properties are a function of only one characteristic frequency, ωₒ, which is equivalent to one characteristic temperature, Θₒ (Debye 1912). The specific heat, Cᵥ, of a Debye solid is defined as (Kittel 1971)

\[ Cᵥ = 3R\frac{\Thetaₒ}{T} \]

where Θₒ is the Debye temperature; R is the gas constant; and \(\frac{d}{dT}(\Thetaₒ/T)\) is the Debye function for specific heat from tables. Most solids of interest to geoscience are not monatomic. Debye theory may be applied usefully to certain polyatomic minerals, provided the vibrational phonon density of states is well approximated by a Debye frequency spectrum (Kittel 1971),

\[ g(\omega) = \omega^2 \quad \omega \leq \omegaₒ \]
\[ = 0 \quad \omega > \omegaₒ \]

where \(\omegaₒ\) corresponds to \(\Thetaₒ\).

Equation 2 does not work as a substitute for the phonon density of states if the solid has a wide band gap, as found in NaI, α-quartz, or calcite. Polyatomic solids in which Equation 2 is a useful substitute for the phonon density of states are called Debye-like solids; these include NaCl, MgO, Al₂O₃, and, as we shall see, MgSiO₃ perovskite. Minerals are rarely Debye-like solids because their thermoelastic properties are not usually a function of a single characteristic temperature. Note that there is no consideration of optic modes in a Debye-like solid.

The pertinent parameters are vₙ and vₛ, the shear and longitudinal sound velocities, and the maximum phonon frequency, ωₒ, (or temperature, Θₒ). The value of Θₒ is found from the sound velocities as given by the relation between Θₒ and the mean sound velocity, vₑ (Poirier 1991)

\[ Θₒ = 251.2 \left(\frac{\mu}{\mu_p}\right)^{1/3} vₑ \]

where \(\mu = M/p\) is the mean atomic mass; M is the molecular mass; \(\mu_p\) is the number of atoms in the vibrating cell (\(\mu_p = 2\) for NaCl or MgO); and p is the density. \(vₑ\), the mean sound velocity, is related to the measured sound velocities by

\[ \frac{3}{vₑ} = \frac{2}{vₙ} + \frac{1}{vₛ} \]

\(vₑ\) is only slightly larger than \(vₙ\), as seen when Equation 4 is written as

\[ vₑ = vₙ \left[\frac{3}{2 + (vₙ/vₛ)^3}\right]^{1/3} \]
Debye theory for polyatomic solids

For polyatomic solids, \( p > 1 \) and the original Debye assumptions are violated; hence the name Debye-like solids, when Equation 1 is empirically obeyed. NaCl is a good example of a Debye-like solid. The value of \( \Theta_o \) determined from acoustics is 316 K at low temperature, whereas the estimate of \( \Theta_o \) determined from calorimetric properties at high \( T \) is 321 K (Barron et al. 1980). The closeness in these values satisfies a requirement of Debye theory. The \( \omega-k \) dispersion curve calculated from lattice dynamics and the resulting \( f(\omega) \) curve for NaCl are plotted in Figure 2 (top), where the maximum lattice frequency is \( \omega_{\text{max}} \). Also shown is the position of \( \omega_o \) from acoustics, called \( \omega_{\text{D}} \), which is close to \( \omega_{\text{max}} \) for NaCl.

The Debye frequency spectrum, \( f(\omega) \), is a parabola (Eq. 2) terminating at \( \omega_{\text{D}} \) found from the experimentally determined \( \nu_m \) with an ordinate such that the area under the Debye curve is equal to the area under the actual phonon distribution curve, \( 3pN \). When the value of \( \omega_{\text{D}} \) is close to that of the phonon dispersion determination of \( \omega_{\text{max}} \), as shown in the top of Figure 2, the thermal properties calculated by Debye theory are close in value to corresponding measured values or to those calculated from the detailed phonon density of states.

NaI is an example of a solid that is not Debye-like. NaI has a wide band gap, and the frequency cutoff, \( \omega_{\text{max}} \), is considerably larger than \( \omega_{\text{D}} \) calculated from the acoustic properties, as shown in Figure 2 (bottom). The phonon density of states shows that almost half the modes have frequencies higher than \( \omega_{\text{D}} \). As a consequence, the specific heat curve, \( C_v \), of NaI approaches the Dulong and Petit limit at much higher temperatures than predicted by the Debye theory.

Lattice dynamics deals with the vibrations of the whole lattice, three times Avogadro's number of vibrations. In this approach, the thermal energy is defined in a statistical sense (Born 1915, 1923; Barron 1955), and the thermoelastic properties are defined in terms of the lattice dynam-
ANDERSON: THERMOELASTICITY OF MgSiO₃ PEROVSKITE

MgO: A DEBYE-LIKE SOLID

The case of MgO illustrates a Debye-like solid. Figure 3 shows the MgO phonon density of states (Sangster et al. 1970). On this plot is placed the Debye frequency, \( \omega_0 \), determined by \( v_0 \) (having been determined by the isotropic averages of both \( v_0 \) and \( v_i \)). It is seen in Figure 3 that for the phonon density of states, the bulk of the optic modes is at frequencies between the high peak at \( 13 \times 10^{12} \) s \(^{-1} \) and \( \omega_0 \), and only a small tail of frequencies exceeds \( \omega_0 \) (19.68 \( \times 10^{12} \) s \(^{-1} \)).

At absolute zero, \( \Theta_D \) should be equal to the thermally determined Debye temperature, \( \Theta_D \), at \( T = 0 \) (Barron 1957). This is indeed the case for MgO. White and Anderson (1966) reported that at absolute zero, \( \Theta_D = 940 \) K, whereas \( \Theta_{D} = 946 \) K. Also Barron (1957) showed that for a Debye solid \( \Theta_D \) and \( \Theta_{D} \) should be equal at high temperature. For MgO, \( \Theta_D \) at 1200 K is 866 K, and Barron (1977) reported from his study of Debye-Waller factors that the caloricométric \( \Theta \) at infinite temperature (\( T > \Theta \)) is near 810 K.

A crucial test for the existence of a Debye-like solid is to calculate \( C_v \) from the Debye theory, then compare it with \( C_v \) computed from the measured \( C_p \), as done in Table 1 for MgO. Data on \( C_v \) from \( C_p \) from 400 to 1700 K in the table are taken from Table 15 in Anderson and Isaak (1995). \( C_v \) computed from the Debye theory, where the acoustic \( \Theta_D \) descends slowly with \( T \), is taken from Table 30 of Anderson and Isaak (1995). In this table we see that \( C_v \) from measured \( C_p \) differs from \( C_v \) calculated from measured sound velocity, exceeds in value most of the optic frequencies in the phonon density of states.
acoustic velocities by less than about 2%, except for the end points.

Except for the end points, this error is within the experimental error of measured thermal expansivity, since

\[ C_v = C_p - \alpha^2 K_c VT. \]  

(6)

It is seen from Equation 6 that the conversion from \( C_v \) to \( C_p \) is sensitive to \( \alpha^2 \), so precise determination of \( \alpha \) is required to find the exact value of \( C_p \) from the measured \( C_v \). Of all the variables measured in Equation 6, \( \alpha \) is often the least well known at high \( T \). Excepting the values at 400 and 1700 K, the agreement is within about 2%. The disagreement at 400 K arises because the Debye theory is often weakest when \( T/\Theta < 0.4 \). This is where the Debye \( C_v \) curve is rising rapidly with \( T \), and a small error in \( T/\Theta \) is greatly multiplied to make the uncertainty in \( C_v \) large. The disagreement at 1700 K arises from the uncertainty in the measured \( \alpha \) at that \( T \). The overall agreement between \( C_v \) (Debye) and \( C_v \) is as good as can be found for most metals and is satisfactory proof that MgO is a Debye-like solid.

In the last column of Table 1 are listed the values of \( C_v \) calculated by Chopelas (1990) from the phonon density of states, as given by Sangster et al. (1970) and shown in Figure 3. The equation used to find \( C_v \) as a function of \( T \) using the phonon density of states, \( g(\omega) \), is

\[ C_v = 3pR \int_0^\infty \frac{e^x}{(e^x-1)} x^2 g(\omega) d\omega \]  

(7)

where \( x = \frac{h\omega}{kT} \). The comparison between \( C_v \) as calculated by the Debye theory, \( C_v \) determined by the experimental data on \( C_v \), and \( C_v \) from the density of states (Eq. 7), is shown in Table 1.

The main feature of the calculation of \( \Theta_p \) for MgO is the steady decrease of \( \Theta_p \) with temperature resulting from the temperature dependence of the sound velocities (plotted in Fig. 4). I depart from customary procedure in that the acoustic data here appropriate to every temperature are used to determine the value of \( \Theta_p \) and in the calculation of \( C_v \) at that temperature. Also plotted in Figure 4 is \( \Theta_p \) vs. \( T \) for two other solids: \( \text{Al}_2\text{O}_3 \) and \( \text{MgO} \). Note that the slopes of \( \Theta_p \) vs. \( T \) are similar for all three minerals.

The assumed variation of \( \Theta_p \) with \( T \) for MgSiO₃ perovskite is shown in Figure 5, plotted as a dashed line. The slope of MgSiO₃ vs. \( T \) is made parallel to the measured slopes of \( \text{Al}_2\text{O}_3 \) and \( \text{MgO} \). The triangle plotted in Figure 5 is from the Brillouin measurements of Yeganeh-Haeri (1994), giving \( v_p \) and \( v_s \), which anchor the low-\( T \) end of \( \Theta_p(T) \). Using specific heat data, Akaogi and Ito (1993) estimate \( \Theta_p \) and its variation with \( T \) from 100 to 400 K, as shown by the dotted line in Figure 5. The Akaogi and Ito estimated value for \( \Theta_p \) at 1000 K is 1030 (20), agreeing well with the value for \( \Theta_p \) at 1027 K at 1000 K.

MgSiO₃ perovskite: another Debye-like solid

The phonon density of states of MgSiO₃ perovskite

The Debye theory customarily is assumed to apply to MgSiO₃ perovskite whenever the thermal energy factor, \( E_n \), in the Mie-Grüneisen expression for thermal pressure
is calculated by the Debye function for internal energy (as was done by Stixrude et al. 1992 and Jackson and Rigden 1996).

Liebermann (1982) calculated successfully the bulk sound velocity, \( v_\text{b} \), of MgSiO\(_3\) perovskite by the formula, \( v_\text{b} \propto \frac{k}{\rho} \), which was derived by Shankland (1972) from Debye theory. The idea that MgSiO\(_3\) perovskite may be a Debye-like solid is certainly not new (Anderson 1995), but it has not yet been proved.

Thus I examine evidence that MgSiO\(_3\) perovskite is a Debye-like solid. The phonon density of states for MgSiO\(_3\) perovskite according to two sets of calculations (Choudhury et al. 1988; Winkler and Dove 1992) is shown in Figure 6. These phonon densities of states are different. The difference does not significantly affect the Debye approximation to the phonon density of states, but it does affect the calculation of moments of the spectrum, so the moment method used to find \( \Theta_\text{D} \) (Anderson 1995) is not to be used for MgSiO\(_3\) perovskite.

The density of states of MgSiO\(_3\) perovskite is similar to that of MgO in two important features. First, the frequencies of the phonon density of states of MgSiO\(_3\) perovskite are, for the most part, less than \( \omega_\text{D} \), with only a small tail of the spectrum lying beyond the acoustic \( \omega_\text{D} \). Second, at low frequencies, the quadratic frequency dependence of the Debye spectrum merges into the solid's phonon density of states. Note that MgSiO\(_3\) perovskite satisfies the quadratic fit at low \( \omega \) as well as does MgO. Therefore we can expect the properties of MgO arising from Debye theory to be a guide for the corresponding properties of MgSiO\(_3\) perovskite.

Figure 7 shows the density of states model of MgSiO\(_3\) perovskite given by Lu et al. (1994). This is a Kieffer-style density of states constructed from data on measured optic modes. This plot shows the position of \( \omega_\text{D} \) as determined by the velocity measurements of Yeganeh-Haeri (1994), which is 720 cm\(^{-1}\). This plot shows that the preponderance of optic modes lies near the mid-region of the spectrum and that few have frequencies larger than \( \omega_\text{D} \). This is further evidence that MgSiO\(_3\) perovskite is likely to be a Debye-like solid. The results of \( C_\alpha(T) \) found by using the \( \Theta_\text{D} \) (T) curve are shown in columns 3 and 4 of Table 2.

From this table it is seen that the Debye values of \( C_\alpha \) for MgSiO\(_3\) perovskite at 300 and 1000 K are 70.66 J/(mol K) and 118.48 J/(mol K). The values (in the same units) at the same temperatures reported by Winkler and Dove (1992) are 85.29 and 119.97. They used Equation 7 with their phonon density of states, shown in Figure 6. This further indicates that the Debye model is fairly good for the quasiharmonic calculation of \( C_\alpha \), provided one focuses on temperatures above 400 K. Data on \( C_\alpha \) of MgSiO\(_3\) perovskite are sparse in the literature, because \( C_\alpha \) apparently has not been measured above 300 K (Akaogi and Ito 1993).

**Calculation of \( C_\alpha(T) \) emphasizing the importance of \( \alpha(T) \)**

Experimental data on \( C_\alpha(T) \) of MgSiO\(_3\) perovskite over a limited range of \( T \) have been presented by Akaogi and Ito (1993). Comparison of \( C_\alpha \) with the Debye model calculations, which give \( C_\alpha \), requires evaluation of the \( \alpha K_\text{D} VT \) correction term in Equation 6. Calculations of \( C_\alpha \) from \( C_\alpha \) are presented in Table 3. Note that at high \( T \), \( C_\alpha \) from this report is substantially lower than that reported.
by Saxena et al. (1993) and by Lu et al. (1994). The difference comes from different values of $\alpha$ used in the correction term, which is sensitive to $\alpha^2$. This difference justifies a discussion on the appropriate values of $\alpha$ that should be used for MgSiO$_3$ perovskite at high $T$.

At the time the Saxena et al. (1993) book and the Lu et al. (1994) paper were written, the values of $\alpha$ for (Mg,Fe)SiO$_3$ perovskite from Knittle et al. (1986) and Mao et al. (1991) were virtually unchallenged, and so they were used by these authors.

But shortly after the publication of these two reports, many experimental papers on $\alpha$ of MgSiO$_3$ perovskite were published (Wang et al. 1994; Utsumi et al. 1995; Funamori et al. 1996). Masuda and Anderson (1995), using the Utsumi et al. (1995) experimental data to evaluate parameters of the Suzuki equation, found $\alpha(T)$. Jackson and Rigden (1996) reported a PV$T$ study of the combined data of Ross and Hazen (1989), Wang et al. (1994), Utsumi et al. (1995), and Funamori et al. (1996), and they recommended values of $\alpha$ for $\alpha(T)$. Chopelas (1996) and Gillet et al. (1996a) found $\alpha(T)$ from their spectroscopic measurements. Anderson et al. (1996) used the Funamori et al. (1996) data on $V(T)$ for MgSiO$_3$, to find $\alpha(T)$ for MgSiO$_3$; the data are listed in Table 3, column 5. All the results for $\alpha(T)$ published by the authors listed in this paragraph essentially agree with one another, and all are substantially lower than the data presented earlier by Knittle et al. (1986) and Mao et al. (1991). These comparisons of $\alpha(T)$ are illustrated in Figure 8. The value used here (see Table 3), $\alpha = 2.58 \times 10^{-5}$ at 800 K, compares well with the Gillet et al. (1996a) value, $\alpha = 2.5 \times 10^{-5}$ at 800 K.

The evaluation of the correction term, $C_r - C_v = \alpha^2 K/T$, is shown in Table 3, in which the values of $\alpha$, $K_v$, $V$, and $V$ are given in detail. It is seen from Table 3 that the correction term when using the Knittle et al. (1986) $\alpha$ data is three times larger at 1600 K than the correction term when using the Funamori et al. (1996) $\alpha$ data.

The value of $K_v$ used in computing the correction term here (column 2, Fig. 3) is found by integrating $(\partial K/\partial T)_p$ vs. $T$ as presented by Jackson and Rigden (1996). This is discussed in detail later.

The value of $C_r$, from the Debye model is shown in Figure 2. In Table 3, the value is 3470 cm$^{-1}$ at 800 K. Because the $C_r - C_v$, correction is known for the respective $\alpha$ data, one can check on the accuracy of various $C_r$ calculations use an underlying quasiharmonic $C_r$. They all do. Gillet et al. (1996a) investigated the possible presence of anharmonicity by finding the effect of temperature on the Raman spectrum of MgSiO$_3$, perovskite up to 300 K and concluded that there was no evidence of intrinsic anharmonicity strong enough to affect the equation of state, even at very high temperatures (see also Gillet 1996). I conclude, therefore, that anharmonicity need not be considered in the expression for the high-temperature $C_v$, and that MgSiO$_3$ perovskite is indeed quasiharmonic. Calcite, on the other hand, is a solid for which an anharmonicity component is required in the $C_v$ analysis (Gillet et al. 1996b). The various $C_v$ models discussed here appear to be similar, but the $C_r - C_v$ correction varies depending on the choice of $K(T)$ and $\alpha(T)$.

### Table 2. MgSiO$_3$ perovskite: $C_v$, and $C_r$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\theta_D$ (K)</th>
<th>$C_v^\alpha$ (GPa)</th>
<th>$C_v^\beta$ (GPa)</th>
<th>$C_v^\gamma$ (GPa)</th>
<th>$C_v^\delta$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1076</td>
<td>3.377</td>
<td>76.7</td>
<td>76.8</td>
<td>80.3</td>
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<tr>
<td>400</td>
<td>1069</td>
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<td>96.5</td>
<td>99.7</td>
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<td>109.7</td>
<td>113.7</td>
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<td>159.8</td>
<td>175.2</td>
</tr>
<tr>
<td>1000</td>
<td>1027</td>
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<td>174.5</td>
<td>193.4</td>
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<tr>
<td>1100</td>
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<td>0.241</td>
<td>165.4</td>
<td>191.9</td>
<td>213.8</td>
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<tr>
<td>1200</td>
<td>1013</td>
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<td>175.0</td>
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<td>1006</td>
<td>0.000</td>
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<td>245.0</td>
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<tr>
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<td>999</td>
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<td>400.7</td>
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<tr>
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<td>232.3</td>
<td>480.6</td>
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</table>

### Table 3. Details of calculation of $C_r - C_v$ correction

<table>
<thead>
<tr>
<th>$K_v$ (GPa)</th>
<th>$V$ (cm$^3$/mol)</th>
<th>$\Delta V/V$</th>
<th>$\alpha^2 K/T$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.53</td>
<td>234.0</td>
<td>0.09</td>
<td>65.0</td>
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<td>4.06</td>
<td>250.2</td>
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</tr>
<tr>
<td>3.22</td>
<td>285.4</td>
<td>0.00</td>
<td>80.0</td>
</tr>
</tbody>
</table>

Note: $\alpha^2 K/T = \alpha^2 K_{VV'} K_{VT}$. 

*From Anderson et al. (1996) using Funamori et al. (1996) data.

**From Saxena et al. (1993) using Knittle et al. (1986) basic data on $K_v$.

$\alpha$ from Jackson and Rigden (1996). 

$\alpha$ from Gillet et al. (1996a) using Utsumi et al. (1995) and Funamori et al. (1996). 

$\alpha$ from Saxena et al. (1993) using Knittle et al. (1986) basic data on $K_v$.
In spite of the fact that the \( C_v - C_p \) correction obscures the value of \( C_v \) for the last three columns in Table 2, the Debye model appears to perform as well as the other models arising from the density of states, which use varieties of the Kieffer spectrum.

**Calculation of entropy**

Navrotsky (1989) used the simplest approximation for the MgSiO\(_3\) perovskite density of states, a simple, one-continuum model, a rectangular box, between 225 and 900 cm\(^{-1}\), and she found that this model led to \( S = 180.9 \) J/(mol·K) at 1000 K. Gillet et al. (1993) replaced Navrotsky's one-continuum model with a two-cell continuum, and from this calculated \( S \) and \( C_v \) for MgSiO\(_3\) perovskite between 225 and 900 cm\(^{-1}\) (a Kieffer approach) and found 235–247 J/mol for the entropy at 1100 K. I calculated 193 J/mol at 1100 K by the Debye method (see Table 4). The Gillet et al. (1993) value of \( C_v \) was 135–136.7 J/(mol·K) at 1100 K; this should be compared with 124.6 J/(mol·K) at 1100 K shown in Table 2. Akaogi and Ito (1993) reported that by using their experimental determinations of \( C_v \), the entropy of MgSiO\(_3\) perovskite is found to be 57.2 J/mol and 185.5 J/mol at 298 and 1000 K, respectively.

I found \( S(300) \) from \( \int_0^{100} \left( C_v/T \right) \) d\( T \) for the range of \( T \) below 300 K using the \( C_v \) data of Akaogi and Ito (1993) measured between 140 and 295 K. By using a short extrapolation near absolute zero, it was found that \( S(300) \) = 57.4 ± 4 J/mol for MgSiO\(_3\) perovskite, close to the Akaogi and Ito (1993) result mentioned above. Thus in my calculation

\[
S(T) = \int_0^T \frac{C_v}{T} \, dT = 57.4 + \int_0^{100} \frac{C_v}{T} \, dT \text{ J/mol.} \tag{8}
\]

The values of \( S(T) \) so calculated are shown in Table 4 under the column heading \( S^{*}\text{(Debye)} \) and in its note \( (p = 5) \). The values of \( S(T) \) reported here also agree well with the reports of Chopelas et al. (1994) and Lu et al. (1994), in that the Debye values are between the other two values, which were based on Kieffer-type models. Thus there is reasonable agreement between the \( S(T) \) from experiment and the \( S(T) \) calculated from \( C_v \) (in turn calculated from the Debye \( C_v \)). Differences in entropy have as an underlying cause the difference in thermal expansivity used in the calculation of the \( C_v - C_p \) correction, as well as different approximations for the density of states.

**CONTROVERSIES OVER \( \alpha(T) \) AND \( (\partial K/\partial T)_p \)**

**The low sets of \( \alpha(T) \) vs. the high sets of \( \alpha(T) \)**

The value of \( \alpha(T) \) chosen from the set of \( \alpha(T) \) values available for MgSiO\(_3\) perovskite has a strong effect on the values of entropy and specific heat, as shown above. The choice of \( \alpha(T) \) has a strong effect on the predicted density distribution of perovskite at lower mantle conditions as well (Jackson 1983; Stixrude et al. 1992).

In the upper set of values of \( \alpha(T) \) found in Figure 8 are those found by Knittle et al. (1986) for Fe-rich MgSiO\(_3\) perovskite, as reported by Saxena et al. (1993) in a table labeled "MgSiO\(_3\) perovskite," and those found by Mao et al. (1991) for an Fe-rich MgSiO\(_3\) perovskite, as graphed by Chopelas (1996). In the lower sets of \( \alpha(T) \) in Figure 8, the data are all for pure MgSiO\(_3\), perovskite (with no Fe). On this basis, one should choose \( \alpha(T) \) measured on a non-Fe-bearing MgSiO\(_3\) perovskite to calculate \( C_v \) and entropy for a non-Fe-bearing MgSiO\(_3\).

I note, however, the importance of the magnitude of \( \alpha(T) \) in determining the composition of the lower mantle. Both Jackson (1983) and Jeanloz and Knittle (1989) emphasized that a large value of \( \alpha \) between 300 and 1700 K leads to a chondritic-like lower mantle, hence not a pyrolitic mantle composition. Zhao and Anderson (1994) showed that the \( \alpha \) values reported by Mao et al. (1991), in contrast to the \( \alpha \) data of Wang et al. (1994), lead to "drastic differences in the fraction of silicate perovskite in a two-phase-mixture lower mantle."

**The high value or the low value of \( (\partial K/\partial T)_p \) for silicate perovskite?**

The experimental values of \( (\partial K/\partial T)_p \) vs. \( T \) are needed to find extrapolated values of the bulk modulus in this paper, in particular, column 4 of Table 3. This brings us squarely against the controversy about this parameter: Authors measuring this parameter are grouped just as in Figure 8. Those whose data on \( \alpha(T) \) are in the upper set of Figure 8 also report a large value of \( (\partial K/\partial T)_p \), where-

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### Table 4. Comparison of entropy at ambient pressure calculated from the Debye model and calculations from Kieffer-like density of states for MgSiO\(_3\) perovskite with vibrational modes

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \theta_K / T )</th>
<th>( S^\alpha ) (Debye) J/(mol·K)</th>
<th>( S^\alpha ) Lu et al.</th>
<th>( S^\alpha ) Chopelas et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>7.233</td>
<td>18.3</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>5.415</td>
<td>30.8</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>4.320</td>
<td>44.1</td>
<td>44.2</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>3.587</td>
<td>57.4</td>
<td>51.4</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>2.673</td>
<td>80.9</td>
<td>74.9</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>2.124</td>
<td>102.5</td>
<td>96.1</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>1.758</td>
<td>121.7</td>
<td>115.0</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>1.497</td>
<td>138.9</td>
<td>131.7</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>1.301</td>
<td>154.4</td>
<td>146.7</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>1.149</td>
<td>168.5</td>
<td>160.3</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>1.027</td>
<td>181.3</td>
<td>172.5</td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>0.927</td>
<td>193.1</td>
<td>183.8</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.844</td>
<td>204.0</td>
<td>194.2</td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td>0.774</td>
<td>214.1</td>
<td>203.8</td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td>0.714</td>
<td>223.6</td>
<td>212.7</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>0.661</td>
<td>232.5</td>
<td>221.1</td>
<td></td>
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<tr>
<td>1600</td>
<td>0.616</td>
<td>240.9</td>
<td>228.4</td>
<td></td>
</tr>
<tr>
<td>1700</td>
<td>0.575</td>
<td>248.9</td>
<td>236.3</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>0.539</td>
<td>256.4</td>
<td>243.3</td>
<td></td>
</tr>
</tbody>
</table>

Note: Same as bottom of Table 3, \( S \) (Debye) \( p = 1 \), \( S \) (Debye) \( p = 1 \) from the standard Debye table.

* \( S \) (Debye) \( p = 5 \) conversion of \( S \) (Debye) \( p = 1 \) to the case of MgSiO\(_3\) perovskite.

† \( S \) Lu et al. (1994) a Kieffer-like density of states model.

‡ \( S \) Chopelas et al. (1994) a Kieffer-like density of states model.
The calculation of the $C_P - C_V$ correction and entropy requires an accurate value of $K_T$ at high temperature, and to find $K_T$ requires an accurate value of $(\partial K_p / \partial T)_p$ because measurements of $K_V$ or $K_T$ do not exist at high $T$. For MgSiO$_3$ perovskite, the values of $(\partial K_p / \partial T)_p$ are reported between −0.020 and −0.028 GPa/K, with the exception of the Stixrude et al. (1992) value, −0.060 GPa/K, on the basis of the Mao et al. (1991) data. I believe the value of $[(\partial K_p / \partial T)_p]$ reported by Stixrude et al. (1992) is much too high. If the Stixrude et al. value of $(\partial K_p / \partial T)_p = -0.06$ GPa/K is used, $K_p(T)$ of perovskite descends very rapidly with $T$ and, at temperatures corresponding to deep within the lower mantle, $K_p(T)$ of MgSiO$_3$ perovskite might approach $K_p(T)$ of MgO (see Fig. 9 of Anderson et al. 1996).

Even when neglecting the Stixrude et al. value, there is still a difference between values of $(\partial K_p / \partial T)_p$ listed in Table 5. I believe this is due to the fact that below the Debye temperature, the value of $[(\partial K_p / \partial T)_p]$ decreases steadily with decreasing $T$ and eventually approaches zero at $T = 0$, similar to the behavior of $C_p$ at $T$ close to zero. I have used the graph showing $(\partial K_p / \partial T)_p$ over a wide temperature range presented by Jackson and Rigden (1996) as the basis for Figure 9, which is adapted from their Figure 6, to emphasize this point.

Authors whose data on $\alpha$ emphasize the lower temperatures report a lower value of $[(\partial K_p / \partial T)_p]$ than do the authors whose data emphasize the upper temperatures. I used the curves of $(\partial K_p / \partial T)_p$ and $(\partial K_p / \partial T)_p$ in Figure 9 to find by integration $K_p(T)$ and $K_T(T)$ from Yeganeh-Haeri's (1994) values of $K_V$ and $K_T$ at 300 K. The values so determined are listed in Tables 3 and 6.

**Additional Thermoelastic Properties of MgSiO$_3$ Perovskite**

With the tabled values of $K_i$, $K_a$, as well as $\alpha$ available as a function of $T$, there are sufficient data for the determination of the Anderson-Grüneisen parameters,

$$\delta_i = -\left(\frac{1}{\alpha K_i}\right)\left(\frac{\partial K_p}{\partial T}\right)_p$$

and

$$\delta_s = -\left(\frac{1}{\alpha K_s}\right)\left(\frac{\partial K_p}{\partial T}\right)_p$$

The values of these parameters are listed in Table 6, columns 3 and 4. $K_p(T)$ can be evaluated at 100 K intervals with the help of the value of $(\partial K_p / \partial T)_p$ found by Jackson and Rigden (1996), $1.4 \times 10^{-4}$ K$^{-1}$. Thus

$$K_p(T) = K_p(300) + 1.4 \times 10^{-4}(T - 300).$$

Values of $T$ are listed in column 5, Table 6. The Grüneisen ratio, $\gamma = \alpha K/V/C_p$, is next evaluated and listed in column 6 of Table 6.
The value of \( q = (\partial \ln \gamma / \partial \ln V) \) can be evaluated from the equation (Anderson 1995).

\[
q = \delta_r - K' + \left( \frac{\partial \ln C_v}{\partial \ln V} \right)_r \cdot (12)
\]

At \( T > \Theta \), the \( (\partial \ln C_v / \partial \ln V) \) term vanishes, so that for \( T = \Theta \), Table 6 shows that \( \delta_r \) is close to \( K'_\Theta \), and thus \( q \) is very close to unity.

The value of \( v_r \) is determined from \( \Theta_{\text{Th}}^n \) by means of Equations 3 and 4 and \( v_r \), from \( K_r \) and \( \rho \), where \( K_r \) comes primarily from the Jackson and Rigden (1996) determination of \( \partial K_r / \partial T \), and \( \rho \) comes from the Funamori et al. (1996) data on \( V(T) \). Through \( v_r \) and \( v_r \), \( v_r \) is determined by \( v_r^2 = K'/(K_p + 4/3 V) \). The variation of Poisson’s ratio with \( T \) is calculated from \( v_r \) and \( K_p \). It is seen from Table 7 that \( \sigma \) varies between 0.224 and 0.238 from 300 to 1800 K, similar to the variation of \( \sigma \) in \( \text{Al}_2\text{O}_3 \). (Anderson and Isaka 1995). The value of the isotropic shear modulus, determined from \( G = \rho v_r^2 \), is listed in Table 7.

**THERMAL PRESSURE IN THE EQUATION OF STATE**

In PVT calculations where a thermal equation of state is used, the contribution to temperature effects comes from the thermal pressure, \( \Delta P_{\text{th}} \). At high \( T \) in the quasi-harmonic approximation, \( P_{\text{th}} \) is proportional to \( T \), and the proportionality parameter is \( \alpha K_r \) (Anderson 1995).

The equation to obtain the thermal pressure using \( \alpha K_r \) (Anderson and Zou 1989), where \( P_{\text{th}} \) is a function of \( V \) and \( T \), is

\[
\Delta P_{\text{th}} = \alpha K_r (T - T_0) - (\partial K_r / \partial V)_t \ln \frac{V}{V_0}. \tag{13}
\]

Jackson and Rigden (1996) correctly pointed out that to obtain \( \Delta P_{\text{th}} \) in \( P-T \) space, Equation 13 is not rigorously correct because of the omission of a small correction term, resulting from going from \( V-T \) space to \( P-T \) space. This term is \( (\partial K_r / \partial T)_p \int_{T_0}^{T} dT \), and Rigden and Jackson (1996) in fact show in their Figure 6 that \( (\partial K_r / \partial T)_p \) is vanishingly small for \( T = \Theta \) and higher temperatures for \( \text{MgSiO}_3 \) perovskite (see also Fig. 9 of this report). It is a fraction of a percent between 300 and \( \Theta \). The double integral term is large at high \( T \), but it is severely depressed by the smallness of \( (\partial K_r / \partial T)_p \), at high \( T \). At low \( T \), where \( (\partial K_r / \partial T)_p \) is just a few percent, the double integral term is small because of the value of \( \alpha \) and the smallness of \( T \). The correction term was evaluated at all temperatures and found to be insignificant in the calculation of \( \Delta P_{\text{th}} \), so that Equation 13 is sufficient even though it is not rigorous.

The value of \( \Delta P_{\text{th}} \) at 1800 K is 10 GPa for \( \text{MgSiO}_3 \) perovskite (Table 6). This is to be compared with \( \Delta P_{\text{th}} \) (1800) = 9.24 for \( \text{Al}_2\text{O}_3 \). (Anderson and Isaka 1995), a value consistent with the change of \( \rho_0 \) for the two solids. According to quasiharmonic theory, in the high-\( T \) approximation, the value of \( \alpha K_r \), which is the coefficient defined by \( (\partial P_{\text{th}} / \partial T)_p \), of silicates with an average mass of 20-21, should increase from mineral to mineral as \( \Theta^{4/3} \). (Anderson 1995). The increase in \( \Theta^{4/3} \) from \( \text{Al}_2\text{O}_3 \) to \( \text{MgSiO}_3 \) perovskite is 5.5%; the increase in the high-\( T \) value of \( \alpha K_r \) is about 5%. This means that the \( \Delta P_{\text{th}}-T \) relationship of \( \text{MgSiO}_3 \) perovskite fits nicely into the pattern of \( \Delta P_{\text{th}} \) vs. \( T \) of rock-forming minerals (Fig. 2.3 in Anderson 1995). This constitutes a cross check on the value of \( \alpha K_r \) at high \( T \).
Using Equation 13, Jackson and Rigden (1996) analyzed the PVT data of MgSiO₃ perovskite from four experiments (Ross and Hazen 1989; Wang et al. 1994; Utsumi et al. 1995; Funamori et al. 1996) and found thermal pressure vs. T. The variation of $\Delta P_T$ vs. T is shown by small circles in Figure 10, which is modified from Figure 5a of Jackson and Rigden (1996). Also plotted in this figure as a solid line is $\Delta P_T$ obtained in this study (listed in the last column of Table 6). In Figure 10, we observe that the calculated Debye value of $\Delta P_T$, found in Table 6, is in agreement with that obtained from experiment, which means that for MgSiO₃ perovskite, the Debye model produces a satisfactory equation of state. In addition, when Equation 13 was replaced by the Mie-Grüneisen term for thermal pressure,

$$\Delta P_T = \gamma \left[ \frac{E(T)}{V} - E(T_o) \right]$$  \hspace{1cm} (14)

(see Fig. 5b of Jackson and Rigden 1996), satisfactory agreement with experiment was also found.

**CROSS CHECKS AND COMPARISON WITH OTHER REPORTS**

$K_s$

$K_s$ was determined from the curve of $(\partial K_s/\partial T)_p$ vs. T as taken from Jackson and Rigden's (1996) Figure 9. $K_s$ could also have been calculated from $K_s = K_p(C_p/C_v)$, but I used this equation as a cross check. From Tables 2 and 4, at 1000 K, $K_s(C_p/C_v) = 255.4$, and from Table 6, as determined from Jackson and Rigden's (1996) $(\partial K_s/\partial T)_p$, $K_s = 254.2$, off by 0.4%. The difference is 0.07% at 500 K. This cross check also constitutes a verification of the Jackson and Rigden (1996) calculations of $K_s(T)$ and $(\partial K_s/\partial T)_p$.

$\delta_r$

I obtain $\delta_r = 5.0$ at 300 K and 4.03 at $T \geq \Theta$. The steady change in $\delta_r$ from $300 < T < 1000$ and the constancy of $\delta_r$ for $T > \Theta$ agree well with what has been found for MgO, Al₂O₃, and MgSiO₃ (Anderson and Isaak 1995) (Fig. 11). The value, $\gamma_0 = 1.5$ at 300 K, was found by Anderson et al. (1995a) in the comparison of isentropes of $\rho$ vs. $P$ for MgSiO₃ perovskite and the adiabat of the mantle, and $\gamma_0 = 1.3$ at room temperature has also been reported by Gillet et al. (1996a). At variance with this data is the report of Stixrude et al. (1992) that $\delta_r = 7$.

The value of $\delta_r$ enables one to compute the value of $\alpha$ at high pressure using the definition of $\delta_r = -(\partial \ln \alpha/\partial \ln \rho)_p$, which upon integration becomes

$$\left( \frac{\alpha}{\alpha_o} \right) = \left( \frac{P}{P_o} \right)^{-\delta_r}.$$  \hspace{1cm} (15)

Let us find $\alpha$ at the conditions, $P = 125$ GPa and 2500 K, where Gillet et al. (1996a) reported $\alpha = 1.1 \times 10^{-3}$ K⁻¹. At these conditions, $\rho_{2500} = 5.49/4.08 = 1.345$. The value of $\delta_r$ at high T is 4.03, according to Table 6, and $\alpha_o$ from the Gillet et al. (1996a) data (see Fig. 8) at 2500 K ($P = 0$) is $3.0 \times 10^{-3}$ K⁻¹. From Equation 15, $\alpha = 0.88 \times 10^{-3}$ K⁻¹, which is below the Gillet et al. value. If we further consider the variation of $\delta_r$ with volume,
the predicted $\alpha$ is somewhat higher. Anderson and Isaak (1993) recommended that $\delta_T$ change with $(\rho/\rho_0)$ as $\delta_T = \delta_T(\rho/\rho_0)^{\kappa}$; when placed in Equation 15, the aforementioned equation for $\delta_T$ gives

$$\frac{\alpha}{\alpha_0} = \exp \left\{ \frac{-\delta_T}{\kappa} \left[ 1 - \left( \frac{\rho}{\rho_0} \right)^{\kappa} \right] \right\}$$

(Anderson and Isaak 1993). Anderson and Isaak (1993) found $\kappa = 1.5$ for MgO, which agrees with the report by Gillet et al. (1996a) that ambient $\delta_T$ decreases to 3.5 at 100 GPa. Using $(\rho/\rho_0) = 0.740$ corresponding to 125 GPa, $\kappa = 1.5$, and the high-$T$ value 4.04 for $\delta_T$, $\alpha = 0.37\alpha_0$ or $\alpha = 1.11 \times 10^{-5}$ K$^{-1}$. This is a good match with the Gillet et al. (1996a) data point; I regard it as a satisfactory cross check on the value of $\delta_T$ at high $T$. 4.03, found in this report. Using the value of $\delta_T$ presented by Stixrude et al. (1992), $\delta_T = 7$, the value of $\alpha$ at 125 GPa and 2500 K would by Equation 15 and by Equation 16 be unreasonably low.

The steady descent of $\gamma$ from 300 to 800 K and the subsequent value at high $T$ being independent of $T$ are consistent with the $\gamma(T)$ behavior of other dense oxides (Anderson and Isaak 1995). The $T = 300$ K value of $\gamma$ found here, 1.52, is consistent with previous estimates that involved the author (Anderson and Masuda 1994; Anderson et al. 1995a). This is to be compared with the Chopelas (1996) value, 1.42, found from spectroscopic measurements in a diamond cell. At high $T$, the value of $\gamma$ reported here is 1.4 and $(\partial \gamma/\partial T)_p = 0$. This value of $\gamma$ is reasonably close to the high-temperature values of Wang et al. (1994) and Gillet et al. (1996a), who both found $\gamma = 1.3$ from their measurements. Jackson and Rigden (1996) found $\gamma = 1.33$ at high $T$. The Utsumi et al. (1995) data on $V(T)$ lead to $\gamma = 1.45$, according to the analysis of Masuda and Anderson (1995). Stacey (1996) found $\gamma = 1.30 \pm 0.09$ for the high-$T$ (2000 K) value of the perovskite structure by the classical method (displacement on pairs of neighboring atoms in the lattice is summed to obtain the net force and the resultant force is made equal to the thermal pressure).

There is, of course, the report by Hemley et al. (1992) that $\gamma = 1.96(9)$, which is at variance with the other reports listed above. It is conceivable that $\gamma$ would be larger for an Fe-rich perovskite than for pure perovskite, but according to Anderson et al. (1996) a thermodynamic constraint prevents $\gamma$ from being greater than 0.5 $K'_V - 0.3$. The Hemley et al. (1992) reported value of $K'_V = 3.9$ requires that $\gamma < 1.6$; thus $\gamma = 1.96(9)$ appears inconsistent with $K'_V = 3.9$.

The Jackson and Rigden (1996) value of $\gamma$, 1.33, determined from a Mie-Grüneisen fit to the $PVT$ data, is slightly less than that shown in Table 6, 1.40 at $T = \Theta$, which was calculated directly from $\alpha$ and $K'_V$ through the definition, $\gamma = \alpha K'_V V/C_V$, but this can be considered as good agreement.

As shown in Table 6 and Figure 7, the value of $q$ is near unity and is exactly unity at 1000 K. Jackson and Rigden (1996) suggested that other properties are not sensitive to the exact value of $q$, so that $q = 1$ was assumed. In this report I find that near $T = \Theta$, $q = 1$ is exact. Gillet et al. (1996a) found $q = 1$, but Hemley et al. (1992) reported $q = 2.5(1.7)$. Cynn et al. (1996) found that for Mg$_2$SiO$_4$, $(\partial \ln C/\partial \ln V)$ rises steadily from 0 to 1 as $T$ decreases from $\Theta$ to 0. Using a straight line for interpolation, the values of $(\partial \ln C/\partial \ln V)$ between 0 < $T$ < 1000 were obtained, giving the values of $q$ to be used in Equation 12 at low $T$. The values of $q$ obtained using the interpolated values of $(\partial \ln C/\partial \ln V)$ are shown in the parentheses of column 7, Table 6 (see Bina 1995 for a discussion of the uncertainty in $q$ from previous studies).

$$\left(\frac{\partial K'_V}{\partial T}\right)_p$$

A plot of this parameter vs. $T$, determined by Jackson and Rigden (1996), is shown in Figure 9. $(\partial K'_V/\partial T)_p$, can
also be determined by the data in Table 6 through the thermodynamic identity,

$$\left(\frac{\partial K_v}{\partial T}\right)_T = \alpha K_v (K_v - \delta_v)$$

(see Anderson 1995, p. 57–58). Because $\alpha K_v$ does not change significantly with $T$ (neglecting the values at 400 K and 500 K), $(\partial K_v/\partial T)_T$ should vary as $K_v - \delta_v$, which is plotted on the bottom of Figure 11. The resemblance between the curve $(K_v - \delta_v)$ determined in this report and $(\partial K_v/\partial T)_T$ determined by Jackson and Rigden (1996) (Fig. 9) constitutes a cross check on the values of $\delta_v$. The value of $K_v - \delta_v$ vs. $T$ from the curve in Figure 11 and the data for $\alpha K_v$ in Table 6 yield, by Equation 17, $(\partial K_v/\partial T)_T = -0.0044$ GPa/K at 300 K, whereas Jackson and Rigden (1996) reported $(\partial K_v/\partial T)_T = -0.005$ GPa/K at ambient conditions. This excellent agreement constitutes a cross check on $(\partial K_v/\partial T)_T$ as determined in this study.

$$\left(\partial P_{\text{tr}}/\partial V\right)_T$$

Because of the identity $(\partial K_v/\partial T) = -V[\partial(\alpha K_v)/\partial V]$, $[(\partial K_v/\partial V)]$ vanishes when $K_v - \delta_v = 0$. But $P_{\text{tr}}$ is proportional to $T$, and $(\partial P_{\text{tr}}/\partial T)_T = \alpha K_v$, so $(\partial P_{\text{tr}}/\partial V)_T$ also vanishes when $K_v - \delta_v$ vanishes (Anderson et al. 1992; Masuda and Anderson 1995). Anderson et al. (1995b) showed from a study on MgO that when $\delta_v = K_v = \pm 0.2$, the thermal pressure is, for all practical purposes, independent of volume. Figure 11 shows that from about 900 K up to 1800 K, $K_v - \delta_v < 1.0$, so the thermal pressure of MgSiO$_3$ perovskite is independent of volume at high $T$. In this regard MgSiO$_3$ perovskite is like Al$_2$O$_3$ and MgO (Anderson 1997). However, the value of the width of the volume zone necessary to satisfy $(\partial P_{\text{tr}}/\partial V)_T = 0$ is not apparent. Nevertheless for high temperatures it appears that one could safely assume that for a reasonably wide compression range, say for $V/V_0$ between 1 and 0.9, the thermal pressure, $P_{\text{tr}}(V_0, T)$, depends only on $T$, not on $V$. This means that the upper part of the curve in Figure 10 does not shift as the volume is changed.

**Conclusions**

It is shown that MgSiO$_3$ perovskite is a Debye-like solid because the specific heat and entropy calculated to high $T$ (1800 K) from Debye theory agree with available experimental data, especially those above 400 K. In this calculation, the thermal expansivity data of Funamori et al. (1996) and the acoustic velocity data of Yeganeh-Haeri (1994) are used as input. It is also shown that a number of thermoelastic properties, including $(\partial K_v/\partial T)_T$, $(\partial K_v/\partial T)_p$, $(\partial K_v/\partial T)_G$, $K_v$, $K_p$, $\delta_v$, $\gamma$, $q$, $v_s$, $v_p$, and $G$, can be calculated and tabulated up to high $T$ once it has been proved that MgSiO$_3$ perovskite is a Debye-like solid. From the calculated properties, $K_v$, $K_p$, $\gamma$, $p$, and $(\partial K_v/\partial T)_T$, the thermal pressure, $\Delta P_{\text{tr}}$, can also be calculated to high $T$. When this is done, the resulting values of $\Delta P_{\text{tr}}$ are shown to agree with $\Delta P_{\text{tr}}$ calculated by Jackson and Rigden (1996) from the existing $PVT$ data set. Thus for MgSiO$_3$ perovskite, Debye theory can be used to obtain the equation of state.

MgSiO$_3$ perovskite joins a small group of Debye-like minerals, now consisting of: MgO, Al$_2$O$_3$, and MgSiO$_3$ perovskite. For this group, the physical properties described above are calculated from data on acoustic sound velocities, ignoring the optic properties. The criterion for selection as a Debye-like solid is that the majority of optic modes occur at frequencies placed toward the center of the phonon density of states, e.g., the Debye frequency is larger in value than the frequencies of the majority of optic modes. By this criterion, other dense minerals, such as stishovite and MgSiO$_3$ ilmenite, are not likely candidates to be Debye-like solids.

Olivine is a near Debye-like solid. Guyot et al. (1996) showed that although Debye theory gives values close to experiment for the properties of $C_v$, $S$, and $\Delta P_{\text{tr}}$ in olivine, the Kieffer approximation to the density of states gives values even closer to experiment.

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