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ON

PHYSICS OF CONDENSED MATTER AT PLANETARY PRESSURES

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A UNIVERSAL THERMAL EQUATION-OF-STATE

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Summary: The experimental evidence is reviewed in support of a law showing a simple linear dependence of thermal pressure on temperature at high T and high P. Data are examined for several classes of solids, including minerals appropriate to planet interiors.

Introduction:

Temperature profiles with depth are of special significance in the description of planet interiors. Many geodynamic investigations of convective processes either require or produce a temperature distribution. A temperature distribution, along with velocity distributions of the convective medium, are deduced by solving the set of differential equations which define the convection. Included in these differential equations is the equation-of-state because it is needed to define the relationships between the thermodynamic variables, V, T, and P. In this paper, attention is focused on the equation-of-state (EOS), which in its most general form is

$$P(V,T) = P_0(V) + P_{TH}(V,T) \quad (1)$$

where $P_0(V)$ is the pressure volume relationship at absolute zero and P_{TH} is the thermal pressure. Consideration of $P_0(V)$ is of minor importance in this paper. $P_{TH}(V,T)$ will be hereafter designated P_{TH} ; the chief concern is its V and T dependence. In the lower mantle P_{TH} is about 12 GPa at 770 km, and about 18 GPa at 2885 km (Anderson and Sumino, 1980). Thus, in the upper portions of the lower mantle, P_{TH} is roughly forty percent of P, and at the core-mantle boundary roughly thirteen percent of P.

Traditionally P_{TH} is given in terms of a Grüneisen parameter, here called γ_M . γ_M is a function of V and (probably) T and the thermal energy E_{TH} . The subscript M identifies γ as the Mie-Grüneisen formulation

$$P_{TH} = \gamma_M E_{TH}/V \quad (2)$$

If (1) and (2) are used as the EOS, then γ_M and E_{TH} have to be defined as functions of V and T either both independently or as a product. The energy equation is

$$E = E_0(V) + E_{TH}(V,T) \quad (3)$$

Thus, the second term of (1) is required to be proportional to the second term of (3). If the range of T and V is large (as found in planet interiors) some difficult theoretical and experimental constraints arise since P is the volume differential of E.

The theory of γ_M has some fundamental problems that appear intractable (Knopoff and Shapiro, 1969; Mulargia and Boschi, 1980). Using (2) for the second term in (1) shall be called the lattice dynamic approach.

Yet in spite of these theoretical difficulties, recent work reported on minerals (Anderson and Suzuki, 1983) and on alkali metals (M.S. Anderson and Swenson, 1983) indicates that empirically the relationship between P_{TH} , T and V is probably quite simple, at temperatures above θ . It is found that

$$P_{TH} = a + bT \quad (4)$$

at high T, where both a and b are virtually independent of V. Now both a and b are measurable quantities, so to the extent that (4) is true, the vexing problem of γ in the high T-low V/ V_0 field is bypassed (Anderson, 1980). Using (4) for the second term in (1) shall be called the thermodynamic approach.

The purpose of this paper is to show that Equation (4) applies to a large class of solids and not just minerals. It in fact applies to alkali metals, alkali solids, noble gas solids, and metals as well as minerals. It seems to hold for all solids which have been carefully tested so far, provided that the focus of attention is restricted to a range of T above the Debye temperature, θ .

If one takes into consideration the effects of a small anharmonic correction at high T, (4) is replaced by

$$P_{TH} = a + bT + cT^2 \quad (5)$$

where cT^2 is the anharmonic correction to the classical quasi-harmonic solid case. Now careful experimentation has shown that cT^2 is often not completely zero, so the solids are really anharmonic. But nevertheless the anharmonic correction is sufficiently small that the cT^2 term can be neglected for most applications, including that of minerals under conditions of planet interiors (that is, the inner planets of the solar system). M.S. Anderson and Swenson (1983) found, for example, for sodium, that P_{TH} is independent of V to within $\pm 10^{-3}$ at compressions up to $V/V_0 = 0.80$, (if $T > \theta$).

They report that P_{TH} is linear in T , where

$$P_{TH} = -0.3805 + .001299T \text{ GPa} \quad (6)$$

between $T = \theta$ and the liquidus.

In some other solids, the anharmonicity is more pronounced than in sodium, but still sufficiently small that it can be neglected in practical calculations.

In geodynamic theories, especially of convection, the neglect of the small anharmonic term, cT^2 , in (5) is probably less serious in the final result than other approximations; such as the assumption of incompressibility, or the assumption that $\alpha\Delta T$ can be neglected, or in assuming linear relationships between viscosity and temperature, or in using two dimensional models rather than three dimensional models, or in the use of low Raleigh numbers in the calculations.

The identification of a and b in (4) comes from the thermodynamic definition of the thermal pressure along an isochore

$$P_{TH} = \int_0^T \left(\frac{\partial P}{\partial T} \right)_V dt \quad (7)$$

Now from identities

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

where α = the thermal expansivity and K_T is the isothermal bulk modulus, and S is the entropy. If αK_T is independent of T , for T above θ , then an approximation to Equation (7) is

$$P_{TH}(T,V) - P_{TH}(\theta,V) = \alpha K_T T \quad (8)$$

Now if P_{TH} is independent of volume (at least within tolerable accuracy) then at $T > \theta$

$$P_{TH} = - \int_0^\theta (\alpha K_T) dT + \alpha K_T T \quad (9)$$

and a and b are readily identifiable by comparing (9) with (4) (Anderson, 1979a).

Now using this thermodynamic approach, α and K_T are each measured versus T by separate experiments, and their product αK_T is b . In the perfect absence of anharmonicity, αK_T is independent of T above θ , but since the measured αK_T sometimes varies slightly, the mean $(\alpha K_T)^*$ is used to identify b . The term

$$a = - \int_0^\theta (\alpha K_T) dT \quad (10)$$

requires the taking of data close to absolute zero, since $\alpha K_T = (\partial P / \partial T)_V$ resembles the classical specific heat function and quantum effects require αK_T to drop at temperatures below θ , and approach absolute zero with a value and slope equal to zero (See Figure 1).

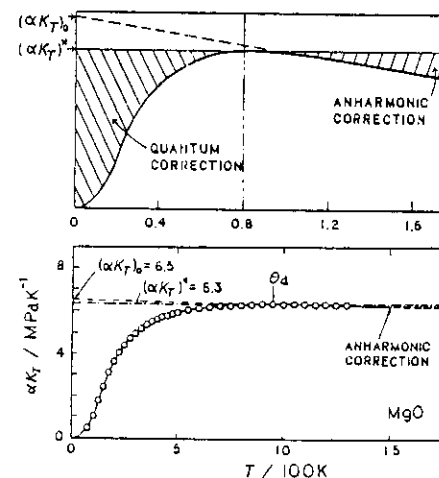


Figure 1. (a) A schematic diagram showing the corrections that must be made to the approximation $(\partial P_{TH} / \partial T)_V = \text{constant}$. The abscissa is T/θ , where θ is the Debye temperature. (b) The data showing αK_T vs T for MgO.

The Debye temperature, θ , has a number of possible interpretations. The acoustic Debye temperature is used here because it does not vary significantly from absolute zero to room temperature. In general, the room temperature value of the acoustic Debye temperature is used for the value of θ . Figure 1 shows the schematic diagram of αK_T vs T indicating the quantum correction and the anharmonic correction to the classical solid core. It also shows the measurements of αK_T for MgO.

For solids which are relatively compressible, direct P , V , and T measurements, if made sufficiently accurate, can be used to find P_{TH} .

Since $P_{TH} = P(V,T) - P(V,0)$, the change in $P_{TH}(V,T)$ with respect to a reference temperature, T^* , is

$$\Delta P_{TH} = P(V,T) - P(V,T^*) \quad (11)$$

The accurate measurements on NaCl by Boehler and Kennedy (1980a) permit the evaluation of (11) on NaCl between 298°K and 773°K ($\theta = 300^\circ\text{K}$), and at compressions down to $V/V_0 = 0.91$ (Anderson, et al., 1982). Table 1 shows the results. Here we see that

Table 1

Change of thermal pressure P_{TH} from room temperature to reference temperature T, $P_{TH}(T) - P_{TH}(25^\circ\text{C})$, at various compressions for NaCl.

V/V_0	$P(\text{GPa})$		$P_{TH}(T) - P_{TH}(25^\circ\text{C}) \text{ (GPa)}$				
	25°C	100°C	200°C	300°C	400°C	500°C	
1.00	0.000	0.216	0.501	0.785	1.067	1.349	
0.99	0.247	0.22	0.500	0.784	1.067	1.348	
0.98	0.509	0.223	0.510	0.783	1.068	1.348	
0.97	0.788	0.215	0.499	0.783	1.069	1.348	
0.96	1.084	0.214	0.499	0.784	1.071	1.348	
0.95	1.398	0.214	0.499	0.786	1.071	1.349	
0.94	1.732	0.214	0.502	0.789	1.078	1.351	
0.93	2.087	0.213	0.502	0.792	1.084	--	
0.92	2.464	0.213	0.50	--	--	--	
0.91	2.864	0.213	--	--	--	--	

Note that P_{TH} is substantially independent of volume. Data computed from Boehler and Kennedy (1980a).

ΔP_{TH} is independent of volume (to within 10^{-3}) and that above θ ,

$$P_{TH} = - .0216 + .00720T \text{ (GPa)} \quad (12)$$

Now, in order to get the results achievable in (11) and (12), the measured isotherms on a P,V plot must be parallel, as they appear for NaCl, in the measured range (e.g., superposition by a translation along the P-axis).

For compressible solids (with bulk modulus values up to that of NaCl), the preferable experiments are made in the static press producing P-V isotherms. For more incompressible solids, the P-V data at high T cannot be measured accurately enough by the static method. Thus for minerals, the measurements of P_{TH} cannot yet be made in a static press. Data on minerals can be obtained by a different route, namely measurements of K_T at high T by resonance measurements, and α at high T by dilatometer

methods (Ohno, I., 1976; Sumino, et al., 1983; Suzuki, et al., 1983; Suzuki, 1975). These measurements are at zero pressure, so indirect thermodynamic methods must be used to evaluate the volume dependence of P_{TH} .

These thermodynamic relationships rely on the identity

$$\left(\frac{\partial \alpha K_T}{\partial V}\right)_T = - \frac{1}{V} \left(\frac{\partial K_T}{\partial T}\right)_V \quad (13)$$

which has been used to evaluate how αK_T depends upon volume for four minerals (Anderson and Suzuki, 1983; Suzuki and Anderson, 1984). The result is that the volume dependence is small and possibly vanishingly small for these minerals. The experimental error for the volume dependence is unfortunately larger than desired, because (13) requires for its evaluation the value of $(\partial K_T / \partial P)_T$ which is not known at high T (see Tables II through V below).

Thermal Pressure for the Alkali Metals.

The ideal experiment for demonstration that P_{TH} is independent of V is to measure pressure vs volume along an isotherm. This experiment is ideal for compressible materials, such as alkali metals.

M.S. Anderson and Swenson (1983) recently measured the compression of sodium, potassium and rubidium from 4.2°K to 300°K, and up to 20 kbar, improving upon the earlier work of this laboratory (Beecroft and Swenson, 1961; Monfort and Swenson, 1965).

Eight isotherms for sodium were taken. The results indicated that the isotherms were essentially parallel (see Figure 2). Analysis of the data shows that the thermal pressure relative to the room temperature value, $P_{TH} - P_{TH}(293^\circ\text{K})$ is independent of volume, at least above the Debye temperature ($\theta = 167^\circ\text{K}$) (also see Figure 2). In this experiment, the conclusion is valid from the sublimation point down to compressions of $V/V_0 = 0.82$. The authors point out that the high temperature data of sodium taken from 373°K to 433°K by Makarenko, et al. (1975), indicate that ΔP_{TH} is independent of volume, except that the volume range of that experiment is from the melting point down to a V/V_0 of about 0.87. Clearly, the thermal pressure is independent of volume

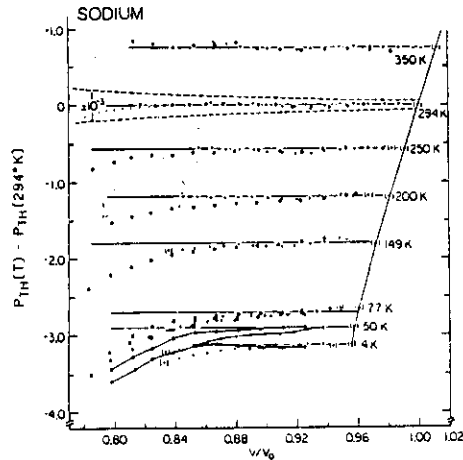


Figure 2. The thermal pressure change $\Delta P_{TH} = P_{TH}(T) - P_{TH}(294^\circ K)$ for sodium, vs V/V_0 (see M.S. Anderson and Swenson, 1983, their Figure 2). Note that to an accuracy of better than 10^{-3} in V/V_0 , ΔP_{TH} is independent of V/V_0 , for temperatures above the Debye temperature $\theta = 167^\circ K$. Two different runs, using different piston diameters, are given by the cross and the filled circle.

at high T . Also, above θ , the thermal pressure is independent of V , even up to the melting point as shown by Figure 3. From the M.S. Anderson and Swenson data, P_{TH} for sodium above θ is given by

$$P_{TH} = 0.0605 + 0.001229T \text{ (GPa)} \quad (14)$$

From Figure 3, we see that (14) is valid right up to the melting point.

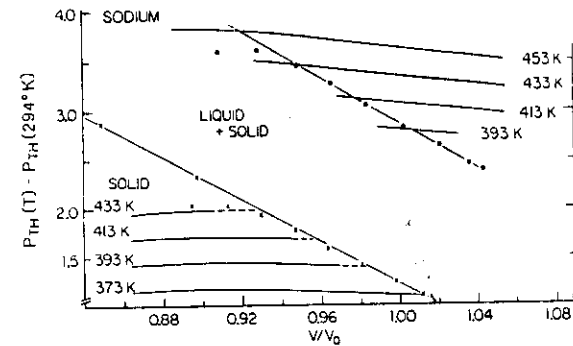


Figure 3. The thermal pressure change $\Delta P_{TH} = P_{TH}(T) - P_{TH}(294^\circ K)$ for sodium, vs V/V_0 at high temperatures (See M.S. Anderson and Swenson (1983), their Figure 6, which is a representation of the results of Makarenko, et al., (1971)). Note that the thermal pressure is virtually independent of V/V_0 right up to the melting line.

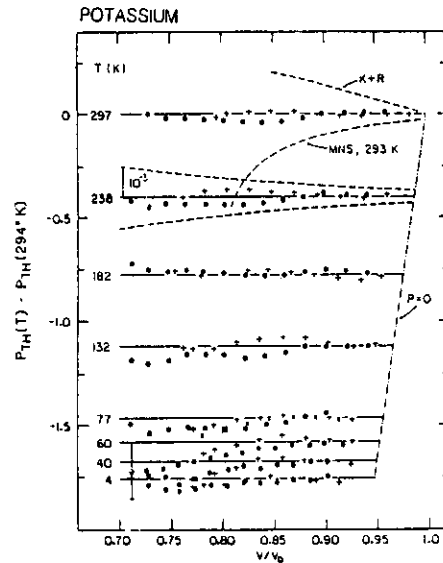


Figure 4. The thermal pressure change $\Delta P_{TH} = P_{TH}(T) - P_{TH}(294^\circ K)$ for potassium, vs V/V_0 (see M.S. Anderson and Swenson (1983), their Figure 9). Note that to an accuracy of better than 10^{-3} in V/V_0 , ΔP_{TH} is independent of V/V_0 for temperatures above the Debye temperature ($\theta = 107.5^\circ K$). Symbols as in Figure 1.

A similar result was found for potassium by M.S. Anderson and Swenson (1983), as shown in Figure 4. Above the Debye temperature ($\theta = 107.5^\circ K$) the thermal pressure is independent of volume to within an error of $\Delta V/V_0 = 10^{-3}$, and this finding holds for volume changes as low as $V/V_0 = 0.70$. Above the Debye temperature, the data fits the straight line

$$P_{TH} = -0.0503 + .00068T \text{ (GPa)} \quad (15)$$

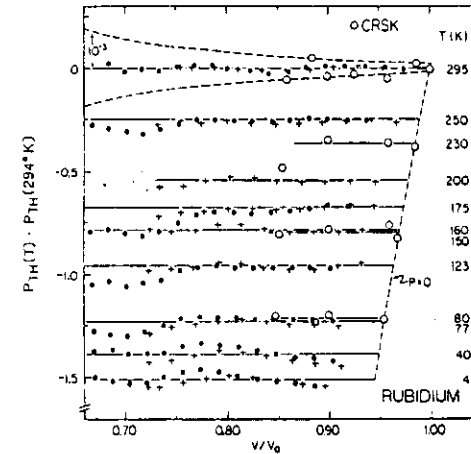


Figure 5. The thermal pressure change, $\Delta P_{TH}(T) - P_{TH}(295^\circ K)$, vs V/V_0 for rubidium, (see M.S. Anderson and Swenson (1983), their Figure 13). Note that to an accuracy of better than 10^{-3} in V/V_0 , ΔP_{TH} is independent of V above the Debye temperature ($\theta = 64.5^\circ K$). Symbols as in Figure 1.

The rubidium data is given in Figure 5 (M.S. Anderson and Swenson, 1983). Again, above the Debye temperature ($\theta = 64.5^\circ K$) the thermal pressure is independent of volume; to better than $\Delta V/V_0 = 10^{-3}$ for compression down to $V/V_0 = 0.75$. Above θ , P_{TH} is linear in T , and the data is represented by

$$P_{TH} = 0.0164 + .000563T \text{ (GPa)} \quad (16)$$

A plot of P_{TH} vs T/θ for the alkali metals is shown in Figure 6, demonstrating linearity above $T = \theta$.

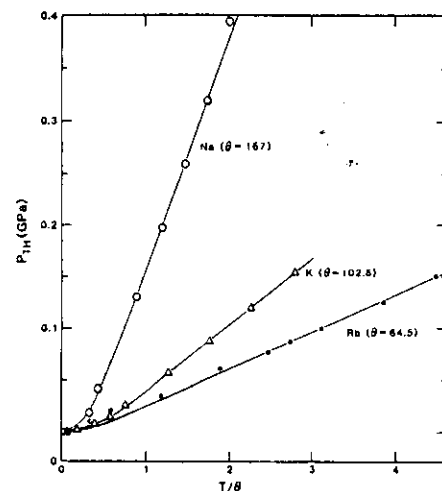


Figure 6. Thermal pressure vs T/θ for three alkali metal solids. Note that P_{TH} is linear with T at high T (above θ) (representation of data given in M.S. Anderson and Swenson (1983)).

Swenson (1966) in an earlier version of the experiment which produced the above alkali halide results, found that for lithium the isochores all superimpose upon the $V = V_0$ isochore at the higher temperatures measured. Thus, the simple linear expression given by (4), is independent of V , for lithium as for the other alkali halides.

It is easy to show that if the thermal pressure is independent of volume along an isotherm, then the thermal contribution to the isothermal bulk modulus, K_T is zero. Thus, the isothermal bulk modulus is independent of T along an isochore

$$(\partial K_T / \partial T)_V = 0 \quad (17)$$

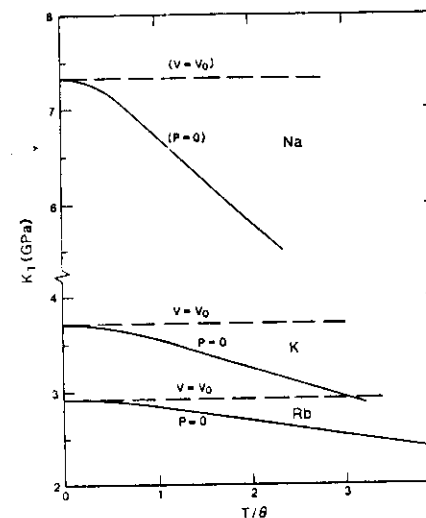


Figure 7. The isothermal bulk modulus, $K_T = V(\partial P / \partial V)_T$, vs T/θ for three alkali metal solids. The solid lines are for constant pressure, and the dashed lines are for constant volume (representation of data given in M.S. Anderson and Swenson, 1983).

The value of $K_T(V = V_0)$ for lithium, sodium, potassium and rubidium is 12.3 ± 0.02 , 7.34 ± 0.05 , 3.703 ± 0.006 , 2.92 ± 0.02 GPa respectively. A plot of the isothermal bulk modulus for the three alkali metals is given in Figure 7. Note that for $P = 0$, K_T decreases with T , but for $V = V_0$, K_T is independent of T .

Comparison of Figure 7 with Figures 2, 3, 4, and 5 underlies a main point of this paper. Whenever $(\partial K_T / \partial T)_V = 0$, the thermal pressure is independent of volume.

For minerals, while it is not possible to measure P_{TH} vs V directly, it is possible to measure or estimate the value of $(\partial K_T / \partial T)_V$.

These data show beyond doubt that for these four alkali metals, Equation (4) is valid wherein the parameters a and b are independent of T and V , within the range of measurement. Similarly, the data on NaCl, Table 1, indicate that Equation (4) also applies wherein the parameters a and b are independent of V and T .

Minerals.

There are two intrinsic difficulties in measuring high temperature thermodynamic properties of minerals. The Debye temperature is considerably above room temperature, and the bulk modulus is high. Because of these combined properties, the static measurement of P , V , T does not have sufficient accuracy for P_{TH} to be evaluated for the data. For minerals with a bulk modulus larger than that of NaCl, the measurement of αK_T as shown in Figure 1 must be used to define P_{TH} .

The high temperature values of αK_T at one bar have been reported by Anderson and Suzuki (1983) and are reproduced in Figure 8. It is seen that the high T value of $(\partial \alpha K_T / \partial T)_V$ over a wide temperature is slightly

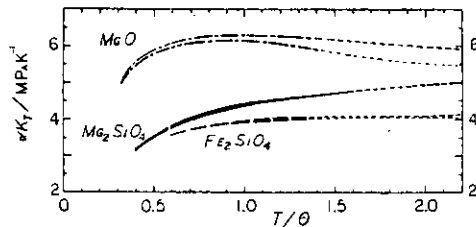


Figure 8. The value of $\alpha K_T = (\partial P / \partial T)_V$ vs T/θ for three minerals at high T (Anderson and Suzuki, 1983). Extrapolations are to mantle temperatures. For the case of forsterite, αK_T is probably not independent of T .

negative for periclase. However, it may be taken for zero for the case of fayalite. For forsterite, the value of $(\partial \alpha K_T / \partial T)_V$ is positive, indicating detectable anharmonicity for this solid.

The plot of αK_T vs T for garnet (Suzuki and Anderson, 1984) shows that at high T , αK_T for this mineral is independent of T (see Figure 9).

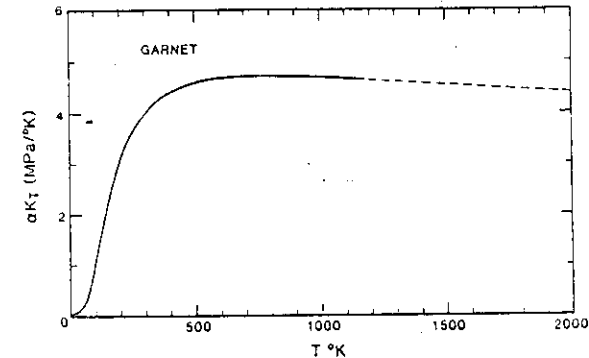


Figure 9. The value of $\alpha K_T = (\partial P / \partial T)_V$ vs T for garnet. Here αK_T is independent of T at high T .

Divergence from linearity of the pressure function, P_{TH} , can be determined and marked by T^* , where $\theta < T < T^*$ is the linear relationship given by Equation (4). For periclase the anharmonic term in Equation (5) is negative and for fayalite it is positive, but for each mineral cT^2 is negligible below some temperature T^* .

Since αK_T is a measured quantity, P_{TH} is found by the integration of laboratory data. Integration suppresses the evidence that αK_T is not exactly constant with T , and an empirical straight line for P_{TH} can be made to fit reasonably all the data. This is shown in Figure 10, where the integrated data for P_{TH} of the four minerals has been plotted along with the data for NaCl determined by the static high pressure method. Careful examination of the line for Mg_2SiO_4 shows there to be a slight curvature upwards.

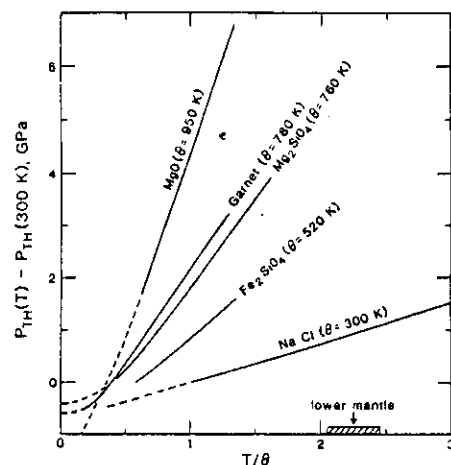


Figure 10. The experimentally determined thermal pressure (relative to the value at room temperature) vs T/θ for five solids measured along an isochore ($V = V_0$). A slight non-linearity is detected in forsterite. For the other solids, P_{TH} vs T is represented by quite straight lines.

For applications to geodynamic problems in the Earth, especially convection, anharmonicity such as suggested in Figure 8 can be ignored. The effect of pressure is to suppress anharmonicity by increasing T^* . The physical interpretation of this phenomena is to be found in the effect of P on the interatomic potential.

Asymmetry of the interatomic potential causes anharmonicity, and this asymmetry arises because of the balance between the attractive forces and the repulsive forces at $P = 0$. As pressure greatly increases, the influence of the attractive forces relative to the repulsive forces diminishes, leading to a diminished anharmonicity.

At high P , the repulsive forces are balanced primarily by the pressure, and the attractive forces are incidental. This idea has been quantified by Hardy (1980). Using his results, it is suggested that when P is, as in the lower mantle of the Earth, the value of T^* is perhaps three times what it is at room pressure. Thus at mantle pressures, we could expect that the isobaric P_{TH} is linear in T at all mantle temperatures, for the four minerals tested so far.

The Volume Effect Upon the P_{TH} Parameters.

Even though increased pressure will increase the lower limit, T^* , of the anharmonicity, it may have other effects on the simple relationship given by Equation (4). If pressure affects the parameter $b = \alpha K_T$, then the various isochores through straight lines may not be parallel. (Note that they are found to be parallel for the four alkali metals and for NaCl.)

One cannot expect the isobars to be parallel at temperatures below the Debye temperature where the solid is not classical. A case in point is the data on LiF, taken by Boehler and Kennedy (1980b). This data (examined by Anderson, et al. (1982)), see Table II, shows that

Table II

Change of $[P_{TH}(T) - P_{TH}(25^\circ\text{C})]$ with temperature T at various compressions for LiF

V/V_0	$P(\text{GPa})$	$P_{TH}(T) - P_{TH}(25^\circ\text{C})$ (GPa)				
		25°C	100°C	200°C	300°C	400°C
1.000	0.000	0.513	1.225	1.963	2.702	
0.995	0.332	0.516	1.226	1.959	2.700	
0.990	0.674	0.516	1.225	1.953	--	
0.985	1.026	0.514	1.223	1.943	--	
0.980	1.389	0.507	1.218	(1.941)	--	
0.975	1.764	0.496	1.21	--	--	
0.970	2.150	0.482	--	--	--	
0.965	2.548	0.464	--	--	--	
0.960	2.959	--	--	--	--	

Note a slight tendency for P_{TH} to decrease with decreasing volume at 100°C .

P_{TH} depends upon V/V_0 for the 100°C, 200°C, 300°C isotherms. One might expect this to occur since these measurements are all taken well below the Debye temperature (700°K).

The test for the pressure effect on the parameter b cannot be made directly for data on incompressible minerals, as it can for NaCl and more compressible solids. In the case of minerals, the test for the possible shift of αK_T with V must be made indirectly by the use of a thermodynamic identity, given by Equation (13).

If K_T vs T at constant V is independent of T , then from Equation (13) we obtain

$$(\partial(\alpha K_T)/\partial V)_T = 0 \quad (18)$$

Now measurements are taken at constant P , not constant V , so to evaluate the right side of (13) from data, we use the following calculus equation:

$$\left(\frac{\partial K_T}{\partial T}\right)_V = \left(\frac{\partial K_T}{\partial T}\right)_P + \alpha K_T \left(\frac{\partial K_T}{\partial P}\right)_T \quad (19)$$

The terms on the right side of Equation (4) are opposite in sign and about the same magnitude, so they may cancel out, satisfying Equation (18). Smith and Cain (1980) made a careful survey of the data on the alkali halides, endeavoring to find if Equation (18) was satisfied, by evaluating the terms in (19). They found that from acoustic data that $(\partial K_T/\partial T)_V$ is a small negative number: for NaCl, $(\partial K_T/\partial T)_V = -0.0014 \text{ GPa/degree}$.

But on the other hand, the data of Boehler and Kennedy (1980a), as indicated by Table 1, shows that the thermal pressure is independent of volume, therefore the thermal bulk modulus should be zero since

$$K_{TH} = -V(\partial P_{TH}/\partial V)_T \quad (20)$$

Thus $(\partial K_T/\partial T)_V$ should be zero since in general

$$K_T(V, T) = K_T(V) + K_{TH}(V, T) \quad (21)$$

From the data on NaCl it appears that the test of $(\partial K_T/\partial T)_V = 0$ is a harsher test than $(\partial P_{TH}/\partial V)_T = 0$.

We wish to know if $(\partial K_T/\partial T)_V = 0$, or at least is small, for the four minerals plotted in Figure 10. From the tables listed in Anderson and Suzuki (1983), the experimental data for $(\partial K_T/\partial T)$ and αK_T vs T at high T is listed. The difficulty is that the data on $(\partial K_T/\partial P)_T = K'_0$ is scarce at $T > \theta$ for minerals.

Only for MgO is K'_0 known near the Debye temperature. Spetzler (1970) reports that the value for K'_0 at 800K is equal to the room temperature value.

The problem is inverted, and the value of the high- T, K'_0 (above θ), is solved from (19) assuming (17) is satisfied, and this computed value is compared with the experimental values of K'_0 reported in the literature at the various temperatures they were measured (see Tables III, IV, and V). Reasonable agreement is found for MgO, Mg_2SiO_4 and garnet, but not for Fe_2SiO_4 .

It is seen that the room temperature value of K'_0 when used in (19) yields the result that $(\partial K_T/\partial T)_P$ is close to zero for the minerals, periclase, forsterite, and garnet, but not for fayalite. The room temperature value of K'_0 shows that $(\partial K_T/\partial T)_P$ should be negative for fayalite, similar to the case found by Smith and Cain for sodium chloride. For some minerals there is some disagreement among the experimentalists as to the

Table III

¹Computation of $(\partial K_T/\partial P)_T$ for MgO such that K_T is independent of volume above $T = \theta$ ($\theta = 940^\circ\text{K}$).

T $^\circ\text{K}$	$(\partial K_T/\partial T)_P$ MPa/ $^\circ\text{K}$	αK_T MPa/ $^\circ\text{K}$	$(\partial K_T/\partial P)_T$ required for (17)	T $^\circ\text{K}$	$(\partial K_T/\partial P)_T$ measured	year
900	-29.5	6.27	4.70	295 ^a	4.49 ^b	1966
1000	-27.5	6.29	4.37	295 ^a	4.27 ^c	1969
1100	-30.0	6.28	4.17	295 ^a	3.89 ^d	1970
1200	-31.6	6.26	5.06	800 ^e	3.91 ^d	1970
1300	-32.4	6.22	5.21	295 ^a	4.13 ^e	1983

(a) Data reported in Anderson and Suzuki (1983).

(b) Anderson and Andreacchi (1966).

(c) Chang and Barch (1969).

(d) Spetzler (1970).

(e) Jackson and Niesler (1982).

Table IV

Computation of $(\partial K_T/\partial P)_T$ for Mg_2SiO_4 such that αK_T
is independent of volume above $T = 0$ ($\theta = 760^\circ\text{K}$)

T °K	$(\partial K_T/\partial T)_P^a$ MPa/°K	αK_T MPa/°K	$(\partial K_T/\partial P)_T$ required for (17)	T °K	$(\partial K_T/\partial P)_T$ measured	year
700	-22.6	4.32	5.16			
800	-22.8	4.43	5.15	100°K	5.39 ^b	1969
900	-23.2	4.52	5.13	100°K	4.99 ^c	1969
1000	-23.5	4.62	5.09			
1100	-23.7	4.70	5.14			
1200	-24.0	4.76	5.04			
1300	-24.2	4.83	5.01			

(a) Data reported in Anderson and Suzuki (1983).

(b) Kumazawa and Anderson (1969).

(c) Graham and Barench (1969).

Table V

Computation of $(\partial K_T/\partial P)_T$ for Fe_2SiO_4 such that αK_T is
independent of volume above $T = 0$ ($\theta = 510^\circ$)

T °K	$(\partial K_T/\partial T)_P^a$ MPa/°K	αK_T MPa/°K	$(\partial K_T/\partial P)_T$ required for (17)	T °K	$(\partial K_T/\partial P)_T$ measured	year
500	-26.3	3.95	6.65	300	5.97 ^b	1971
600	-26.9	4.02	6.70			
700	-27.1	4.06	6.74	300	4.98 ^c	1983
800	-27.4	4.09	6.70			
900	-27.5	4.10	6.70			

(a) Data reported in Anderson and Suzuki (1983).

(b) Chung (1971).

(c) Schwab and Graham (1983).

value of K_0' . So the experimental uncertainty, at room T, is probably at least ± 0.5 . Add to that the uncertainty between the room temperature and high temperature values, and an uncertainty in K_0' about ± 1.0 is indicated for data in Equation (19), as shown in Figure 11.

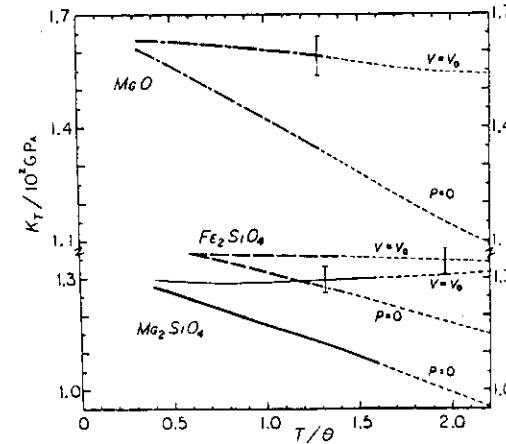


Figure 11. The temperature dependence of isothermal bulk modulus K_T in relation to the normalized temperature T/θ for three minerals showing solutions for constant pressure ($P = 0$), and constant volume ($V = V_0$) (Anderson and Suzuki, 1983). The error bar at 1000°K indicates the range of K_T caused by an estimated error of ± 1.0 in value of $(\partial K_T/\partial P)_T$ at high temperature. Compare this figure with that of the alkali halides, Figure 6.

The data for K_T vs T , under the conditions of $P = 0$, and $V = V_0$, are plotted in Figure 11. No definite conclusion can be made, but it appears that a reasonable case can be made for assuming that $(\partial K_T/\partial T)_V = 0$, and therefore the slope of the thermal pressure curve, Equation (4), may be taken as invariant with pressure.

Anderson and Sumino (1980) inverted the seismic data of the Earth's lower mantle and compared the results of experiments with data on the thermal expansivity of minerals. In this way the thermal pressure of the lower mantle was estimated. The data were too insensitive to prove, one way or the other, that the thermal pressure is independent of volume. One possible solution using the

thermal model of Brown and Shankland (1981) indicated that P_{TH} of the mantle was close to that of MgO , and that (18) was satisfied. Another possible solution using the thermal model of Stacey (1977), indicated that the b term in Equation (4) could be slowly decreasing with P (see Figure 9 of Anderson and Sumino, 1980), and that (18) was not satisfied.

In view of all the evidence, it appears that it is a reasonably good assumption for minerals at high T to assume Equation (4), where the parameters are independent of V , as the link between P and T in the EOS.

The Noble Gas Solids.

The measurements on noble gas solids (M.S. Anderson and Swenson, 1983) are especially instructive since they cover data for the solids up to near the liquidus. Their experiments covered the range of P up to 2 GPa and from 4.7°K up to near the triple point in each case. The compressions are relatively large, going down to V/V_0 near 0.8. They analyzed their data for P_{TH} , and found $(\partial P/\partial T)_V = \alpha K_T$ to be independent of both V and T for all three solids.

Of special interest to geophysical problems is the temperature dependence of K_T at constant V (see Equation (13)). Their experiments clearly showed that $(\partial K_T/\partial T)_V$ is not small below θ , but above θ the isochores of K_T were parallel to the T -axis. A good case in point is solid argon, where their data only extended to 80°K; the Debye temperature is 100°K. Their data for K_T is reproduced in Figure 12. As expected $(\partial K_T/\partial T)_V$ has a rather large negative slope. For the case of solid krypton, where $\theta = 65^\circ K$, the data extend to 120°K and are plotted in Figure 13. Here, above about 80°K, the values of K_T are parallel with the T -axis. For the case of solid xenon, where $\theta = 55^\circ K$, the data taken up to 160°K, are plotted in Figure 14. We see that the isochores of K_T are indeed parallel to the T -axis. The values of $(\partial P/\partial T)_V$ are .00235, .00220 and .00177 GPa/° for solid argon, solid xenon, and solid krypton.

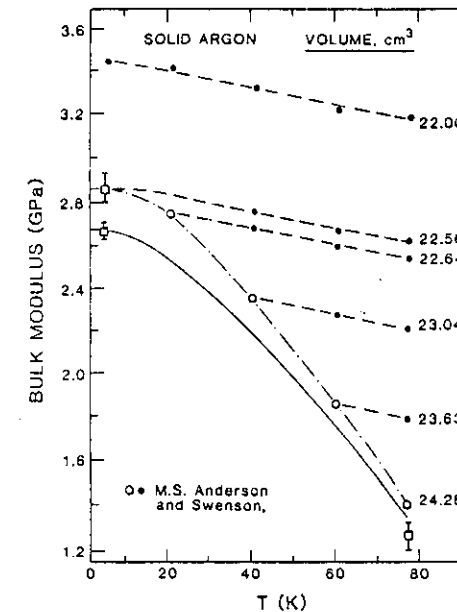


Figure 12. The temperature and volume dependence of K_T of solid argon (M.S. Anderson and Swenson, 1975). Dashed lines show the isochores. Note that the isochores of K_T are not parallel to the T -axis, but also note that the data is below the Debye temperature ($\theta = 100^\circ$).

Table IV

Computation of $(\partial K_T/\partial P)_T$ for Mg_2SiO_4 such that αK_T is independent of volume above $T = \theta$ ($\theta = 760^\circ\text{K}$)

T $^\circ\text{K}$	$(\partial K_T/\partial T)_P^a$ $\text{MPa}/^\circ\text{K}$	αK_T^a $\text{MPa}/^\circ\text{K}$	$(\partial K_T/\partial P)_T$ required for (17)	T $^\circ\text{K}$	$(\partial K_T/\partial P)_T$ measured	year
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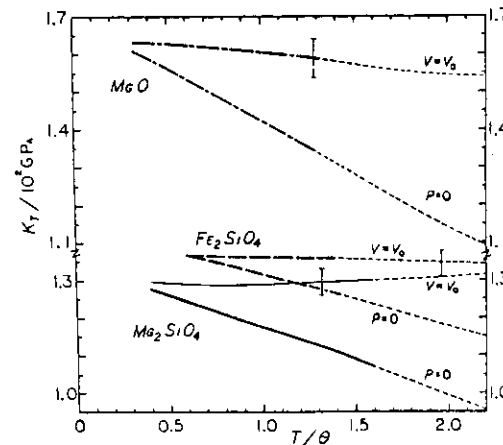


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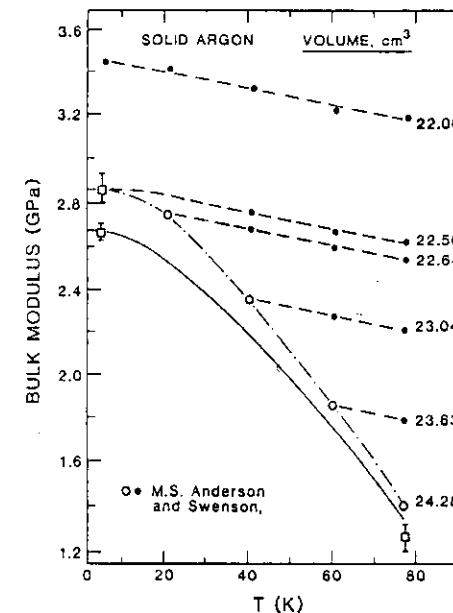


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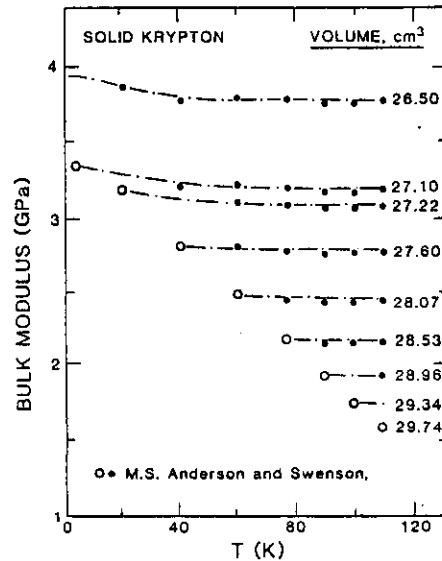


Figure 13. The temperature and volume dependence of K_T of solid krypton (M.S. Anderson and Swenson, 1975). The isochores of K_T are parallel with the T-axis above the Debye temperature ($\theta = 65^\circ\text{K}$).

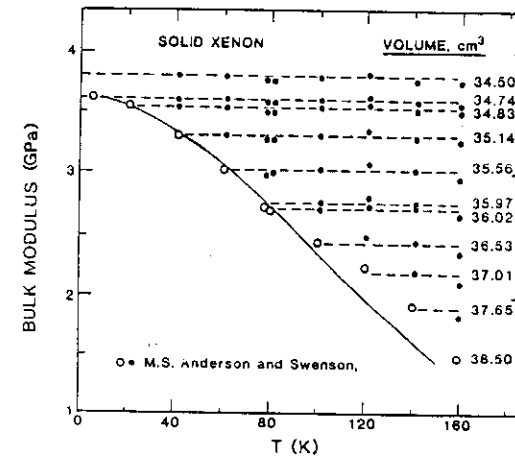


Figure 14. The temperature and volume dependence of K_T of solid xenon (M.S. Anderson and Swenson, 1975). The isochores of K_T are parallel with the T-axis above the Debye temperature ($\theta = 55^\circ\text{K}$).

The application of the solid noble gas data to Equation (4) indicates that the parameter b is independent of volume, but the parameter a is not, being worse for solid argon and best for solid xenon. This situation may arise from the fact that the zero point energy is not insignificant for the noble gas solids below the sublimation line. Of special interest is solid argon, where the data extend right to the melting point, showing the anharmonicity of the pressure function may be small right up to melting.

Metals.

Swenson analyzed the data on copper in a review article (Swenson, 1968). His data on copper is reproduced here as Figure 15. The behavior of K_T and K_S both at

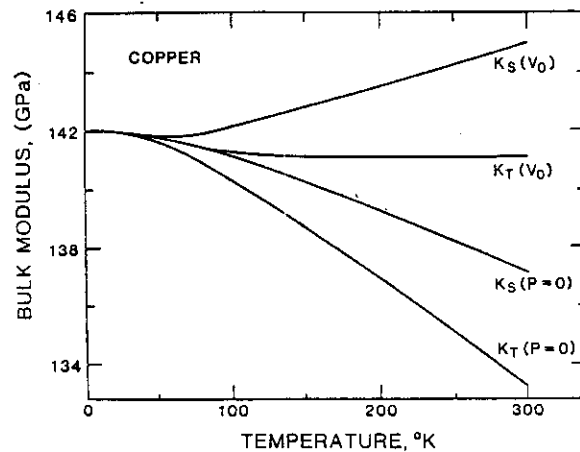


Figure 15. The temperature dependence of the bulk modulus for copper (Swenson, 1968). Note that above 150°K, the isochoric K_T is parallel with the T-axis ($\theta = 150^\circ\text{K}$).

$P = 0$ and $V = V_0$ describes the general situation. It is clear that for copper, the isochoric K_T is virtually parallel to the T-axis. Nevertheless, there are some indications that the calculated value of $(\partial K_T / \partial T)_V$ is not exactly zero, although it is small (Swenson, 1968). The crude data available in the 1968 paper suggests that other metals (Ag, Au, Al, Fe, Ta) follow the pattern of Cu.

Summary of the Data.

It is shown that the high temperature behavior of P_{TH} and K_T are quite similar for at least three classes of solids: noble gas solids, alkali metals, possibly alkali halides as suggested by the data of one member, NaCl, and possibly metals as suggested by copper. The thermal pressure is independent of volume and linear in temperature, or very nearly so, over the measured range. In the solids, where θ is near room temperature or lower, the ideal experimental set up is in a static press where V is measured vs controlled T and P .

Of significance is the measurement on sodium metal, where P_{TH} has been measured right up to the solidus. Figure 3 shows that P_{TH} is independent of volume and

linear in T up to the melting point; e.g., no anharmonicity is observed in P_{TH} even just below melting.

In the case of minerals, such direct measurement is not possible. However, it is shown that the measured value of $\alpha K_T = (\partial P / \partial T)_V$ at one bar above θ has some of the same characteristics as found for the other solids listed above. There is a tendency of αK_T to be independent of T at high T , and the departures from this independence would disappear at high pressure.

In the case of the alkali metals, the data show that when the isochoric values of K_T are parallel to the T-axis, whereby $\alpha K_T = (\partial P / \partial T)_T$ is independent of volume, such as is expected from the thermodynamic identity, (14). For the minerals measured so far, the data indicate also that αK_T is probably independent of V , although exact proof requires knowledge of K_0' at temperatures above the Debye temperature, a measurement currently beyond experimental reach.

Swenson's Law.

The fact that the same behavior of the thermal EOS has been found for so many different kinds of solids indicates that we are dealing with a correspondence principle which transcends solid type, and is probably independent of the chemical bond type and the crystallographic class.

Much yet remains to be done to prove conclusively that minerals have the same behavior as these other solids. The data taken so far on four such minerals indicate that their thermal EOS is of the same type as the alkali metals, noble gas solids, and alkali halides.

The fact that $(\partial K / \partial T)_V$ is close to zero at high T for so many solids cannot be just a coincidence. The evidence is now sufficient that future research in this field will no doubt concentrate on finding solids with a significant departure from (17) as special cases.

The approximation $(\partial K_T / \partial T)_V \approx 0$ may be regarded as a beginning point in the equation-of-state of solids, just as the ideal gas law, $PV = nRT$ is regarded as the beginning point in the equation-of-state of gases. The ideal gas law is approximately true for solids over an extended V, T space. Perhaps future theory for thermodynamics of solids will use (17) as a first order effect in expressions having higher order terms.

Following the analogy of the ideal gas law, we can expect (17) to be less and less true as V/V_0 approaches a small number. Our data base now indicates that the V/V_0 range for (17) is probably 1 to 0.75 for temperatures above θ . Thus, we might reasonably expect to use (17) in theories of the Earth's lower mantle, and possibly in the Earth's core, but we should not be surprised if it failed substantially under high shock wave pressures where $V/V_0 < 0.5$, or for compressions in the rocky cores of the major planets.

Before the publication of the recent precise data on alkali metals (Figures 2 through 7) and on minerals (Figures 8 through 10), I proposed (Anderson, 1979a) on the basis of the then existent data that (17) be called "Swenson's law." The recent experiments described above which have much improved accuracy confirms the importance of (17).

Swenson did not originate the idea of using (17) as a test for solids. That credit apparently goes back to Lazarus (1947). Nor should we overlook the importance of the work of C.S. Smith and his colleagues who from 1954 to 1980 stressed the calculation of (17) as clarifying certain points in the thermodynamics of solids. Work from Swenson's laboratory, from 1955 until today, emphasized the importance of (17) to the EOS; first as a way of describing a set of P,V,T data with a few simple statements, and second, by showing how P,V,T static data could be drawn closer to the ultrasonic or resonance experimental contributions to the EOS.

If Swenson's law, $(\partial K_T / \partial T)_V = 0$, is valid over a bounded region $[0 < T < T^*, V_0 < V < V']$, then within that region, all P,V,T data is determinable by $P(V, T_0)$ and $V(T)$ at $P=0$. That is with an isothermal compression run at room temperature and the isobaric experimental expansivity at room pressure. In this case, the isotherms are parallel [superposition by a shift along the volume axis] and the thermal pressure is linear with T and independent of volume.

Conversely, if $\alpha K_T = (\partial P / \partial T)_V$ is independent of T between 0 and T^* , then P_{TH} is linear with T in that temperature region. Further, if $(\partial K_T / \partial T)_V$ is independent of T, then the thermal pressure is independent of V. With knowledge of the P_{TH} function and one isotherm (at room temperature, for example), the P,V,T field can be reconstructed between $0 < T < T^*$ and for volume changes down to the smallest volume measurement, but the accuracy depends upon the accuracy of $(\partial K_T / \partial P)_T$ used in finding $(\partial K_T / \partial T)_V$.

Volume and Temperature Dependence of the Grüneisen Parameter, γ .

The EOS approach in this paper does not use γ in thermodynamic calculations. However, this approach can be used to evaluate γ . Consider the volume dependence of the Grüneisen parameter taken from

$$\gamma = \alpha K_T V / C_V \quad (22)$$

and

$$(\gamma / \gamma_0) = (V / V_0)^q \quad (23)$$

where q is presumed independent of T and V.

Bassett, et al. (1968) followed by Roberts and Ruppin (1970), have shown that (22) and (23) yield

$$q = 1 - \frac{1}{\alpha K_T} \left(\frac{\partial K_T}{\partial T} \right)_P - \left(\frac{\partial K_T}{\partial P} \right)_T - \left(\frac{d \ln C_V}{d \ln V} \right) \quad (24)$$

Using $d \ln C_V / d \ln V = \gamma (d \ln C_V / d \ln T)$ (Smith and Cain, 1980), we have

$$q = 1 - \delta_T - \left(\frac{\partial K_T}{\partial P} \right)_T - \left(\frac{\gamma d \ln C_V}{d \ln T} \right) \quad (25)$$

If $\delta_T = (\partial K / \partial P)_T$ and $\partial C_V / \partial T = 0$, then $q = 1$. Thus we see that it does not automatically follow that q is exactly one when $(\partial K_T / \partial T)_V$ is exactly zero: the anharmonicity of C_V comes into the calculation.

High T data exists on the three minerals (forsterite, fayalite and periclase), sufficient to evaluate (25). From the C_V data, we find that $d \ln C_V / d \ln T = 0.15$ at very high temperatures (above θ) (Anderson and Suzuki, 1983).

Applying (25) and using the data on δ_T from Anderson and Suzuki (1983), it turns out that $q = 5.5 - (\partial K / \partial P)_T$, MgO; $4.27 - (\partial K / \partial P)_T$, Mg_2SiO_4 ; $5.82 - (\partial K / \partial P)_T$, Fe_2SiO_4 . Thus q is about unity for MgO, less than unity for forsterite and greater than unity for fayalite.

Boehler (1983) found from direct compression experiments that $q \approx 1$ for olivine and magnesium oxide. Brown and Shankland (1981) found, using their thermal model, that $1.0 < q < 1.5$ satisfied the seismic data of the lower mantle of the Earth, while Stacey's (1977) thermal model requires that $q < 1$ for the lower mantle. Anderson (1979b) found $q = 1.5 \pm 0.7$ for the lower mantle.

The variation of γ with T at high T, both at constant P and constant V, has been presented for fayalite, forsterite, periclase and garnet (Anderson and Suzuki, 1983 and Suzuki and Anderson, 1984). They showed that the data on α and K at high T indicated that

$$(\partial \gamma / \partial T)_V = 0 \quad (26)$$

for these four solids.

Variation of the Value of $(\partial P/\partial T)_V$
From Solid to Solid.

An interesting result is that the value of $\alpha K_T = (\partial P/\partial T)_V$ is correlated with the Debye temperature, θ . Solids with small θ have correspondingly small values of $(\partial P/\partial T)_V$. This empirical result is shown in Figure 16. The data for the Earth's lower mantle are plotted, where θ is taken from Anderson (1979b) and the data for αK_T is taken from Anderson and Sumino (1980).

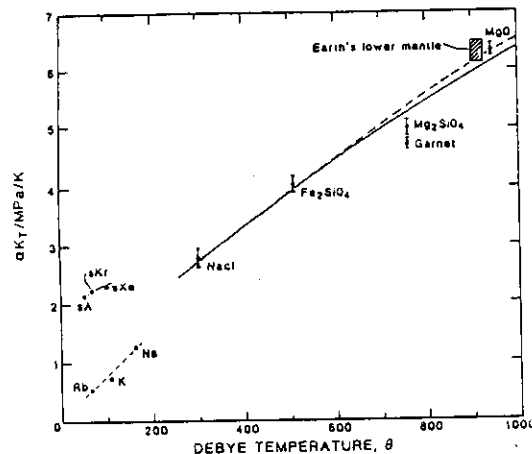


Figure 16. The variation of $(\partial P/\partial T)_V = \alpha K_T$ at high T with the Debye temperature for minerals, alkali halides, and solid noble gases. Data for the Earth's lower mantle lies close to that of MgO.

Conclusions.

Little error is made by assuming that the EOS is given by Equations (1) and (4) for convection theories of planet interiors. Such error as might be made is small compared to other approximations currently made in theoretical geodynamic models of convection, such as the approximation of incompressibility, or the approximation of negligible thermal expansivity ($\alpha \Delta T = 0$), or the use of a modestly high Raleigh number.

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