

Analysis of volume expansion data for periclase, lime, corundum and spinel at high temperatures

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Abstract. We have presented an analysis of the volume expansion data for periclase (MgO), lime (CaO), corundum (Al₂O₃) and spinel (MgAl₂O₄) determined experimentally by Fiquet *et al* (1999) from 300K up to 3000K. The thermal equation of state due to Suzuki *et al* (1979) and Shanker *et al* (1997) are used to study the relationships between thermal pressure and volume expansion for the entire range of temperatures starting from room temperature up to the melting temperatures of the solids under study. Comparison of the results obtained in the present study with the corresponding experimental data reveal that the thermal pressure changes with temperature almost linearly up to quite high temperatures. At extremely high temperatures close to the melting temperatures thermal pressure deviates significantly from linearity. This prediction is consistent with other recent investigations. A quantitative analysis based on the theory of anharmonic effects has been presented to account for the nonlinear variation of the thermal pressure at high temperatures.

Keywords. Volume expansion; thermal equation of state; thermal pressure; geophysical minerals.

1. Introduction

The volume–temperature data under isobaric conditions particularly at $P = 0$ are of basic importance for investigating the thermoelastic properties of minerals at high temperatures and high pressures (Petukhov and Chekovskoi 1972; Anderson and Masuda 1994; Anderson *et al* 1995a,b). The high temperature cell parameters of periclase (MgO), lime (CaO), corundum (Al₂O₃) and spinel (MgAl₂O₄) at room pressure have been determined from 300K up to 3000K by Fiquet *et al* (1999) with the help of X-ray diffraction experiments using synchrotron radiation. The volume–temperature data measured by Fiquet *et al* are considered to be more accurate and have been found to agree closely within 0.1 % with the thermal expansion data reported by Dubrovinsky and Saxena (1997) in case of MgO (Jacobs and Oonk 2001). In order to understand the variation of volume with temperature for various minerals, we need a thermal equation of state based on the concept of thermal pressure.

Recently, Singh (2002) studied the relationships between thermal pressure and volume expansion with temperature using three different forms of phenomenological equations (Suzuki *et al* 1979; Shanker *et al* 1997; Shanker and Kushwah 2001). A critical test of these equations can be performed with the help of volume–temperature data reported by Fiquet *et al* (1999). In the present study, we consider the four minerals studied by Fiquet *et al* for a wide range of temperatures. For performing the calculations conveniently, we

assume that the thermal pressure changes linearly with temperature. However, the results obtained in the present study would indicate that the thermal pressure starts to deviate from linearity at very high temperatures approaching melting temperatures for the minerals under study. The nonlinear variation of thermal pressure at high temperatures can be explained by taking into account the effect of anharmonicity.

2. Thermal equation of state

According to Anderson (1995), the equation of state can be expressed in terms of thermal pressure as follows

$$P(V, T) = P(V, T_0) + \Delta P_{\text{th}}, \quad (1)$$

where $P(V, T_0)$ represents the isothermal pressure–volume relationship at $T = T_0$, the initial temperature. ΔP_{th} is the difference in the values of thermal pressure at two temperatures, i.e.

$$\Delta P_{\text{th}} = P_{\text{th}}(T) - P_{\text{th}}(T_0). \quad (2)$$

At zero pressure, i.e. at $P(V, T) = 0$, (1) can be written in the following forms

$$-\Delta P_{\text{th}} = P(V, T_0), \quad (3)$$

$$-\left(\frac{V}{V_0}\right) \Delta P_{\text{th}} = \left(\frac{V}{V_0}\right) P(V, T_0), \quad (4)$$

$$-\left(\frac{V}{V_0}\right)^2 \Delta P_{\text{th}} = \left(\frac{V}{V_0}\right)^2 P(V, T_0), \quad (5)$$

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where V_0 is the volume at $T = T_0$ and $P = 0$. The right hand sides of (3)–(5) can be expanded in powers of $(V - V_0)$ in a Taylor series. We can expand f , a function of volume, as follows:

$$f = f_0 + \left(\frac{df}{dV}\right)_0 (V - V_0) + \frac{1}{2} \left(\frac{d^2f}{dV^2}\right)_0 (V - V_0)^2 + \dots \quad (6)$$

Terms up to quadratic in $(V - V_0)$ are retained. The subscript 0 represents the values of derivatives at $V = V_0$ and $T = T_0$. Three functions for f given by the right hand sides of (3)–(5) are considered here. Using the expansion given by (6) we get the following expressions

$$\Delta P_{th} = K_0 \left(\frac{V}{V_0} - 1\right) - \frac{1}{2} K_0 (K'_0 + 1) \left(\frac{V}{V_0} - 1\right)^2, \quad (7)$$

$$\Delta P_{th} = \left[K_0 \left(\frac{V}{V_0} - 1\right) - \frac{1}{2} K_0 (K'_0 - 1) \left(\frac{V}{V_0} - 1\right)^2 \right] / \left(\frac{V}{V_0}\right), \quad (8)$$

$$\Delta P_{th} = \left[K_0 \left(\frac{V}{V_0} - 1\right) - \frac{1}{2} K_0 (K'_0 - 3) \left(\frac{V}{V_0} - 1\right)^2 \right] / \left(\frac{V}{V_0}\right)^2, \quad (9)$$

where K_0 and K'_0 are isothermal bulk modulus and its pressure derivative both at $P=0$. Equations (7)–(9) correspond to (3)–(5), respectively and are quadratic equations in $[(V/V_0) - 1]$. On solving these equations we get the following expressions for volume expansion in terms of thermal pressure

$$\frac{V}{V_0} - 1 = \frac{1}{(K'_0 + 1)} \left\{ 1 - \left[1 - \frac{2}{K_0} (K'_0 + 1) \Delta P_{th} \right]^{1/2} \right\}, \quad (10)$$

$$\frac{V}{V_0} - 1 = \frac{A_1}{A_2} \left[1 - \left(1 - \frac{2A_2 \Delta P_{th}}{A_1^2} \right)^{1/2} \right], \quad (11)$$

where $A_1 = K_0 - \Delta P_{th}$ and $A_2 = K_0 (K'_0 - 1)$.

$$\frac{V}{V_0} - 1 = \frac{B_1}{B_2} \left[1 - \left(1 - \frac{2B_2 \Delta P_{th}}{B_1^2} \right)^{1/2} \right], \quad (12)$$

where $B_1 = K_0 - 2\Delta P_{th}$, and $B_2 = K_0 (K'_0 - 3) + 2\Delta P_{th}$.

Equations (7) and (10) were derived by Shanker *et al* (1997) by expanding the lattice potential energy in powers of $(V - V_0)$ in the form of Taylor series expansion. Equations (8) and (11) have been obtained by Singh (2002) using the method of expanding the product of pressure and

volume in power series of $(V - V_0)$ originally due to Suzuki *et al* (1979). Equations (9) and (12) have been obtained by Shanker and Kushwah (2001) by expanding the product $P(V)^2$ in the powers of $(V - V_0)$. In fact, (10)–(12) can be obtained, respectively from the Taylor Series expansion for P , PV , and $P(V)^2$ in powers of change in volume $(V - V_0)$ due to the rise in temperature. At $P = 0$, the expansion of volume is controlled by thermal pressure and therefore, (7)–(12) represent different forms of relationship between volume expansion (V/V_0) and thermal pressure.

3. Thermal pressure and anharmonicity

Now we can calculate the values of volume expansion, V/V_0 , with the help of (10)–(12) provided the values of thermal pressure are known. It is evident from (1) that $P(V, T_0)$ is a function of volume only along an isotherm $T = T_0$, we can write

$$\left(\frac{dP}{dT}\right)_V = \left(\frac{dP_{th}}{dT}\right)_V \quad (13)$$

where $P = P(V, T)$. Now using the thermodynamic identity

$$\left(\frac{dP}{dT}\right)_V = \alpha K_T, \quad (14)$$

where α is thermal expansivity and K_T the isothermal bulk modulus. From (13) and (14), we have

$$\left(\frac{dP_{th}}{dT}\right)_V = \alpha K_T. \quad (15)$$

It is known that the product αK_T remains nearly constant for most of the solids at higher temperatures $T \geq \theta_D$, the Debye temperature (Anderson 1995). We can, therefore, integrate (15) to obtain

$$\begin{aligned} \Delta P_{th} &= \int_{\theta_D}^T \alpha K_T dT \\ &= \alpha K_T (T - \theta_D), \end{aligned} \quad (16)$$

As an empirical finding, ΔP_{th} is linear in T down to much lower temperatures than θ_D , and we usually find empirically that the data satisfy (Anderson and Isaak 1995)

$$\Delta P_{th} = \alpha K_T (T - T_0), \quad (17)$$

where $T_0 = 300\text{K}$. Equation (17) can be used to calculate the values of ΔP_{th} at different temperatures starting from room temperature provided the values of α and K_T corresponding to Debye temperature are taken for each solid as input. The values of α and K_T for the four solids under study at temperatures close to θ_D are given in table 1. The calculated values of ΔP_{th} are given in tables 2–5. Values of volume expansion V/V_0 are calculated with the help of (10)–(12) using the

values of ΔP_{th} . The input data on K_0 and K'_0 at $T = 300\text{K}$ are also given in table 1. The results for MgO, CaO, Al₂O₃ and MgAl₂O₄ are given in tables 2–5. We note from these tables that the values of volume expansion V/V_0 calculated in the present study are in good agreement with the experimental data reported by Fiquet *et al* (1999) for the four minerals under study. In case of MgO and CaO, (10) of Shanker *et al* (1997) yields imaginary values at very high tempe-

ratures close to the melting temperature T_m . This point has already been noted earlier by Shanker *et al* (1999) and found it useful for developing a criterion of melting. The Singh–Suzuki (11) and Shanker – Kushwah (12) yield the results for V/V_0 in fair agreement with the experimental data. Equations (7)–(9) provide a method for calculating the values of thermal pressures, ΔP_{th} , at different temperatures using the experimental data on V/V_0 reported by Fiquet *et al* (1999).

Table 1. Values of input data (Anderson 1995) for MgO, CaO, Al₂O₃ and MgAl₂O₄. Thermal expansivity, α and isothermal bulk modulus, K_T both are taken at $T = \theta_D$, the Debye temperature.

	MgO	CaO	Al ₂ O ₃	MgAl ₂ O ₄
K_0 (GPa)	161.6	110.6	252	207.9
($T = 300\text{ K}$)				
K'_0 ($T = 300\text{ K}$)	4.15	4.85	3.99	4.18
α ($10^{-5}/\text{GPa}$)	4.38 ($T = 900\text{ K}$)	3.92 ($T = 700\text{ K}$)	2.73 ($T = 1000\text{ K}$)	2.85 ($T = 900\text{ K}$)
K_T (GPa)	144.3 ($T = 900\text{ K}$)	102.3 ($T = 700\text{ K}$)	231.4 ($T = 1000\text{ K}$)	187.3 ($T = 900\text{ K}$)

Table 2. Values of thermal pressure based on (16) and values of V/V_0 calculated from (a) (10), (b) (11), (c) (12) and (d) (16) of experimental data (Fiquet *et al* 1999).

$T(\text{K})$	MgO				
	$\Delta P_{th}(\text{GPa})$ (16)	(a)	(b)	(c)	(d)
300	0	1	1	1	1
421	0.777	1.0049	1.0049	1.0049	1.0044
505	1.308	1.0083	1.0083	1.0083	1.0088
591	1.852	1.0118	1.0118	1.0118	1.0119
694	2.503	1.0162	1.0161	1.0161	1.0163
790	3.110	1.0203	1.0203	1.0203	1.0193
874	3.641	1.0240	1.0240	1.0239	1.0245
964	4.209	1.0281	1.0280	1.0280	1.0279
1052	4.766	1.0321	1.0321	1.0320	1.0343
1120	5.195	1.0353	1.0352	1.0352	1.0369
1211	5.770	1.0398	1.0396	1.0395	1.0412
1281	6.213	1.0432	1.0430	1.0429	1.0479
1446	7.256	1.0518	1.0514	1.0511	1.0522
1664	8.634	1.0639	1.0631	1.0626	1.0609
1738	9.101	1.0683	1.0672	1.0666	1.0682
1773	9.323	1.0704	1.0692	1.0686	1.0674
1873	9.955	1.0767	1.0751	1.0743	1.0709
1901	10.13	1.0785	1.0768	1.0759	1.0803
2036	10.98	1.0878	1.0852	1.0839	1.0853
2153	11.72	1.0965	1.0929	1.0912	1.0930
2262	12.41	1.1053	1.1004	1.0982	1.0982
2373	13.11	1.1154	1.1085	1.1056	1.0998
2473	13.75	1.1257	1.1162	1.1126	1.1075
2573	14.38	1.1379	1.1244	1.1198	1.1169
2673	15.01	1.1535	1.1332	1.1274	1.1248
2773	15.64	1.1826	1.1427	1.1353	1.1360
2873	16.22	-	1.1521	1.1428	1.1420
2973	16.85	-	1.1633	1.1515	1.1456

Table 3. Values of thermal pressure based on (16) and values of V/V_0 calculated from (a) (10), (b) (11), (c) (12) and (d) (16) of experimental data (Fiquet *et al* 1999).

$T(\text{K})$	CaO				
	$\Delta P_{th}(\text{GPa})$ (16)	(a)	(b)	(c)	(d)
300	0	1	1	1	1
398	0.392	1.0036	1.0036	1.0036	1.0055
500	0.800	1.0074	1.0074	1.0074	1.0075
585	1.140	1.0106	1.0106	1.0106	1.0113
688	1.552	1.0147	1.0147	1.0146	1.0163
778	1.912	1.0183	1.0182	1.0182	1.0195
875	2.300	1.0223	1.0222	1.0222	1.0265
1001	2.804	1.0276	1.0275	1.0275	1.0328
1116	3.264	1.0326	1.0325	1.0324	1.0385
1222	3.688	1.0375	1.0373	1.0371	1.0423
1289	3.956	1.0406	1.0403	1.0402	1.0456
1390	4.360	1.0455	1.0451	1.0449	1.0500
1427	4.508	1.0473	1.0469	1.0467	1.0522
1485	4.740	1.0503	1.0498	1.0495	1.0553
1548	4.992	1.0535	1.0529	1.0526	1.0573
1573	5.092	1.0549	1.0542	1.0538	1.0598
1673	5.492	1.0603	1.0594	1.0589	1.0600
1773	5.892	1.0661	1.0648	1.0641	1.0655
1873	6.292	1.0721	1.0705	1.0696	1.0717
1973	6.692	1.0786	1.0763	1.0752	1.0767
2073	7.092	1.0856	1.0825	1.0810	1.0835
2173	7.492	1.0931	1.0890	1.0871	1.0879
2273	7.892	1.1015	1.0959	1.0934	1.0974
2373	8.292	1.1111	1.1032	1.0999	1.1009
2473	8.692	1.1225	1.1111	1.1068	1.1058
2573	9.092	1.1376	1.1195	1.1141	1.1130
2673	9.492	-	1.1288	1.1217	1.1193
2773	9.892	-	1.1392	1.1297	1.1274

Table 4. Values of thermal pressure based on (16) and values of V/V_0 calculated from (a) (10), (b) (11), (c) (12) and (d) (16) of experimental data (Fiquet *et al* 1999).

T(K)	Al ₂ O ₃				
	ΔP_{th} (GPa) (16)	(a)	(b)	(c)	(d)
300	0	1	1	1	1
382	0.504	1.0020	1.0020	1.0020	1.0009
407	0.654	1.0026	1.0026	1.0026	1.0039
583	1.710	1.0069	1.0069	1.0069	1.0063
637	2.034	1.0082	1.0082	1.0082	1.0084
694	2.376	1.0097	1.0097	1.0097	1.0099
731	2.598	1.0106	1.0106	1.0106	1.0109
787	2.934	1.0120	1.0120	1.0120	1.0116
884	3.516	1.0145	1.0145	1.0145	1.0128
919	3.726	1.0154	1.0154	1.0154	1.0136
988	4.140	1.0172	1.0172	1.0171	1.0176
1089	4.746	1.0198	1.0198	1.0198	1.0217
1217	5.514	1.0232	1.0232	1.0232	1.0248
1351	6.318	1.0269	1.0268	1.0268	1.0300
1457	6.954	1.0298	1.0297	1.0297	1.0323
1579	7.686	1.0333	1.0332	1.0331	1.0375
1656	8.148	1.0355	1.0353	1.0353	1.0383
1821	9.138	1.0403	1.0401	1.0400	1.0429
1890	9.552	1.0424	1.0422	1.0420	1.0446
1976	10.07	1.0450	1.0447	1.0446	1.0488
2080	10.69	1.0482	1.0479	1.0477	1.0509
2242	11.66	1.0534	1.0529	1.0527	1.0593

Table 5. Values of thermal pressure based on (16) and values of V/V_0 calculated from (a) (10), (b) (11), (c) (12) and (d) (16) of experimental data (Fiquet *et al* 1999).

T(K)	MgAl ₂ O ₄				
	ΔP_{th} (GPa) (16)	(a)	(b)	(c)	(d)
300	0	1	1	1	1
408	0.583	1.0028	1.0028	1.0028	1.0028
492	1.028	1.0050	1.0050	1.0050	1.0039
585	1.521	1.0075	1.0075	1.0075	1.0079
715	2.210	1.0109	1.0109	1.0109	1.0095
877	3.069	1.0154	1.0154	1.0154	1.0128
986	3.646	1.0184	1.0184	1.0184	1.0175
1114	4.325	1.0221	1.0220	1.0220	1.0213
1257	5.083	1.0262	1.0262	1.0261	1.0257
1363	5.645	1.0294	1.0293	1.0293	1.0293
1497	6.355	1.0335	1.0334	1.0333	1.0316
1589	6.842	1.0363	1.0362	1.0361	1.0357
1691	7.383	1.0395	1.0394	1.0393	1.0382
1791	7.913	1.0428	1.0426	1.0424	1.0409
1889	8.432	1.0460	1.0457	1.0456	1.0429
1927	8.634	1.0473	1.0470	1.0468	1.0442
2056	9.317	1.0517	1.0513	1.0510	1.0510
2191	10.03	1.0565	1.0559	1.0556	1.0566
2288	10.55	1.0600	1.0593	1.0589	1.0573

4. Conclusions

Values of ΔP_{th} thus calculated for MgO, CaO, Al₂O₃ and MgAl₂O₄ are compared in figures 1–4 along with the values of ΔP_{th} estimated from (17) according to which ΔP_{th} varies linearly with temperature. In case of Al₂O₃ (figure 3) and MgAl₂O₄ (figure 4), the variations of ΔP_{th} with temperature are quite linear. The range of temperatures considered for these two solids is only up to 2300K. However, in case of MgO and CaO for which the maximum temperature goes up to about 3000K, the plots showing the variations of ΔP_{th} with T become nonlinear at temperatures $T > 2000$ K (figures 1 and 2). It is evident from these figures that the thermal pressure deviates substantially from linearity at very high temperatures approaching the melting temperatures ($T_m = 3073$ K for MgO and $T_m = 2853$ K for CaO). This deviation from linearity is such that the actual values of thermal pressures become considerably less than the corresponding values predicted from the linear relationship. This prediction is consistent with the recent studies (Wang and Reeber 1996; Jacobs and Oonk 2001; Taravillo *et al* 2002; Popov and Borodai 2005). Wang and Reeber, have found that $(\partial P_{th}/\partial T)_V$ does not remain constant, i.e. the thermal pressure does not change linearly with T at high temperatures. They have shown that $[\partial (P_{th}V)/\partial T]_V$ remains almost constant with temperature at high T . This is related to the observation that the product of thermal expansivity, α and isothermal bulk modulus, K_T , decreases slowly but significantly at high T (Shanker *et al* 1999; Jacobs and Oonk 2001). According to Wang and Reeber (1996), the product $\alpha K_T V$ remains nearly constant at high T . Since the volume, V , increases by about 10–15% in case of MgO and CaO (tables 2 and 3) in the temperature range 2500–3000K, the values of αK_T should decrease by the same amount for this temperature range. This would imply from (17) that the actual values of thermal pressure should be smaller by about 10–15%. It is worth mentioning here that when we use the smaller values of ΔP_{th} in the temperature range 2500–3000K, the Shanker (10) yields real values for V/V_0 up to the temperatures approaching T_m . At $T \approx T_m$, (10) yields imaginary values for V/V_0 . Equation (10) has been used by Shanker *et al* (1999) and Wang *et al* (2000, 2001) for studying the high pressure melting of ionic solids and geophysical minerals.

An analysis of the non-linearity of thermal pressure at high T can be presented by taking into account the effect of anharmonicity. The first three anharmonic terms arising from the strong temperature-induced motions contribute to the Helmholtz energy as follows (Landau and Lifshitz 1958; Wallace 1972)

$$F_{anh} = A_1(V)T^2 + A_0(V) + A_{-2}(V)T^{-2}, \quad (18)$$

where the coefficients A_1 , A_0 and A_{-2} are the functions of volume only. The anharmonic contribution to the thermal pressure is found by using the relationship

$$P = - \left(\frac{\partial F}{\partial V} \right)_T, \quad (19)$$

which gives the following additional terms to thermal pressure

$$(P_{th})_{anh} = - \left[\frac{\partial A_1}{\partial V} T^2 + \frac{\partial A_0}{\partial V} + \frac{\partial A_{-2}}{\partial V} T^{-2} \right]. \quad (20)$$

These additional terms should be added in the linear relationship for thermal pressure given by (17) to obtain ΔP_{th} at high T . The last term in (20) is negligibly small at high T and the second term is independent of T . Only the first term in (20) contributes to the non-linearity of thermal pressure at high T . This quadratic dependence of ΔP_{th} on T has been found by Wallace (1972). The following quadratic expression is

obtained in the high temperature limit of the quasi-harmonic approximation (Anderson and Isaak 1995)

$$\Delta P_{th} = \overline{\alpha K_T} (T - T_0) [1 - \alpha (T - T_0)], \quad (21)$$

where $\overline{\alpha K_T}$ is the value of product taken at temperature close to the Debye temperature (table 1). Equation (21) can be used to estimate the values of ΔP_{th} provided we know the values of thermal expansivity, α , at high temperatures. Values of α in case of MgO and CaO have been reported by Singh and Chauhan (2002) up to very high temperatures close to their melting temperatures. Values of ΔP_{th} calculated from (21) are shown in figures 1 and 2 for MgO and CaO, respectively.

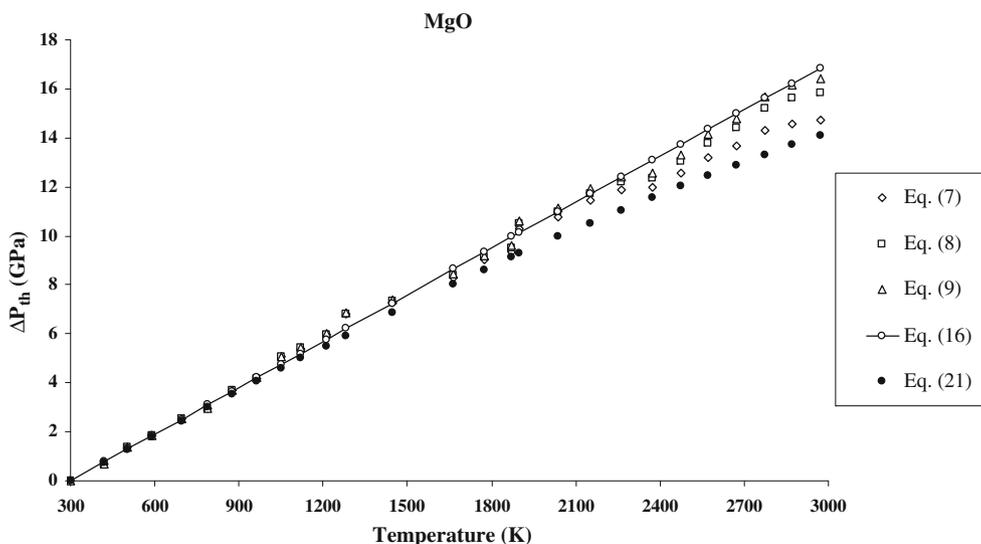


Figure 1. Plots between thermal pressure, ΔP_{th} and temperature, T . Values of thermal pressure are obtained from (7)–(9) using experimental data on V/V_0 , and compared with the values based on (16) (straight line).

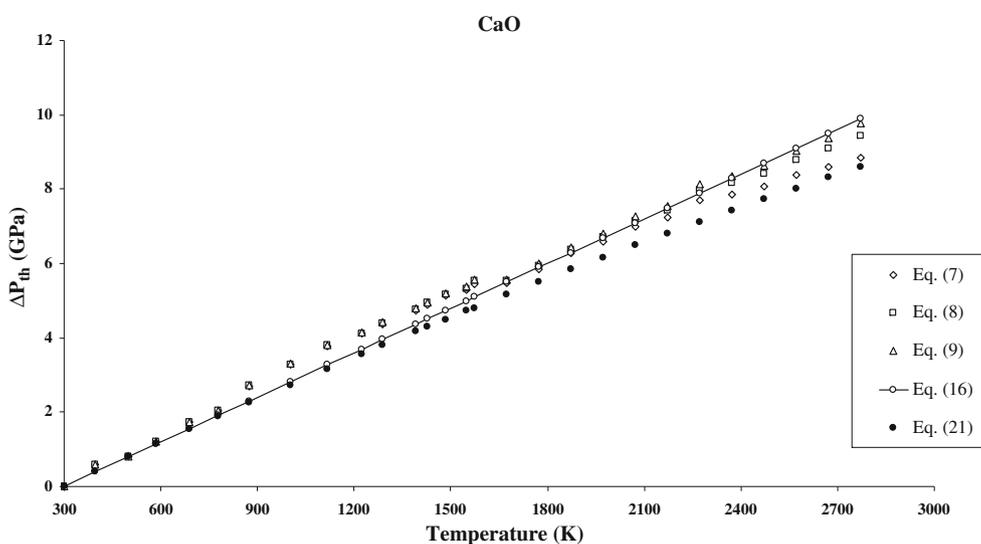


Figure 2. Plots between thermal pressure, ΔP_{th} and temperature, T . Values of thermal pressure are obtained from (7)–(9) using experimental data on V/V_0 , and compared with the values based on (16) (straight line).

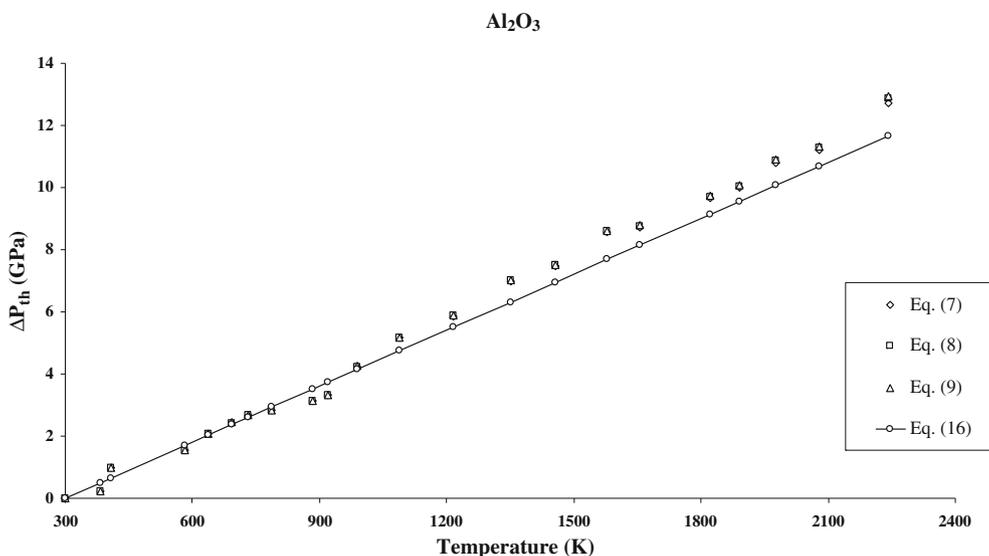


Figure 3. Plots between thermal pressure, ΔP_{th} and temperature, T . Values of thermal pressure are obtained from (7)–(9) using experimental data on V/V_0 , and compared with the values based on (16) (straight line).

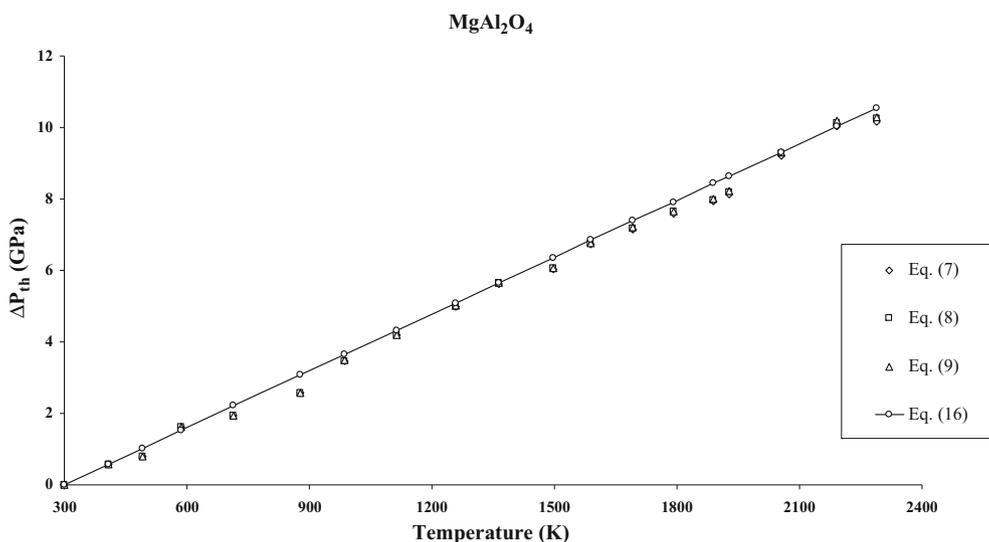


Figure 4. Plots between thermal pressure, ΔP_{th} and temperature, T . Values of thermal pressure are obtained from (7)–(9) using experimental data on V/V_0 , and compared with the values based on (16) (straight line).

It is revealed from these figures that the nonlinear variation of thermal pressure, ΔP_{th} , predicted in (21) is very similar to that obtained from the thermal equation of state (7). This provides strong evidence that the non-linearity of thermal pressure at high T originated from the anharmonic effects.

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