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An equation of state applied to sodium chloride and caesium chloride at high pressures and high temperatures

Mithlesh Kumari and Narsingh Dass

Physics Department, University of Roorkee, Roorkee 247667, India

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Abstract. In the present paper, an equation of state is proposed which has been found to be applicable at high pressures and high temperatures. The proposed equation of state has been used to compute the pressure–volume behaviour, the isothermal bulk modulus and its pressure derivative, the coefficient of thermal expansion and the Anderson–Grüneisen parameter of NaCl and CsCl at high pressures (up to 400 kbar) and high temperatures (up to 1073 K). The results obtained for $V(P, T)/V(0, T)$ are found to be in very good agreement with Decker's data in the whole ranges of pressure and temperature. Further, the other calculated results are also found to be in good agreement with the experimental data. The present calculations definitely lend support to the proposed equation of state and to the method used to extend the applicability at higher temperatures.

1. Introduction

In principle, all the thermodynamic properties of a system can be predicted once precise knowledge of the interatomic forces becomes known, but the imprecise knowledge of the interatomic forces along with the limitations of the procedure to carry through the prediction compel us to use simplifying models and approximations to obtain an equation of state. In support of the statement, some examples can be given here: the equations of state obtained by Murnaghan (1949, 1951), Keane (1954) and Birch (1952).

With the advancement in high-pressure physics, there has been extensive experimental and theoretical work to determine the equation of state. However, even for a simple substance such as sodium chloride a reliable theoretical equation of state cannot be predicted owing to lack of precise knowledge of the interatomic potential. Moreover, the results depend strongly on the kind of model and the input data used for calculation.

Therefore the purpose of the present paper is

- (i) to propose an equation of state which is applicable to high pressures and
- (ii) to calculate the isothermal bulk modulus and its pressure derivative along with the Anderson–Grüneisen parameter and coefficient of thermal expansion at various pressures (up to 400 kbar) and at elevated temperatures (up to 1073 K).

To apply the proposed equation of state, we choose solid sodium chloride and caesium chloride because extensive compression data for both these solids have been given by Decker (1971). Moreover, sodium chloride is widely used as an internal pressure standard in high-pressure x-ray studies.

2. Theory

To obtain the equation of state, we assume that the ratio of second to first pressure derivatives of the isothermal bulk modulus $B_T(P, T)$ is a pressure-independent quantity, i.e.

$$[\partial^2 B_T(P, T)/\partial P^2]_T / [\partial B_T(P, T)/\partial P]_T = -Z. \quad (1)$$

The successive integration of equation (1) within the limits $P = 0$ and $P = P$ give the following equations:

$$B'_T(P, T) = B'_T(0, T) \exp(-ZP) \quad (2)$$

$$B_T(P, T) = B_T(0, T) + [B'_T(0, T)/Z][1 - \exp(-ZP)] \quad (3)$$

and

$$\ln[V(P, T)/V(0, T)] = -(1/\eta) \ln\{1 + [B'_T(0, T)/B_T(0, T)Z][1 - \exp(-ZP)]\} - ZP/\eta \quad (4)$$

where $\eta = B_T(0, T)Z + B'_T(0, T)$ and $B'_T(0, T)$ is the first pressure derivative of bulk modulus $B_T(0, T)$ at $P = 0$.

The following results can be easily obtained from equations (1)–(4).

(i) The volume decreases continuously with increasing pressure and becomes zero as the pressure tends to infinity.

(ii) The bulk modulus $B_T = -V(\partial P/\partial V)_T$ increases continuously with increasing pressure and has a finite value equal to $[B_T(0, T) + B'_T(0, T)/Z]$ as $P \rightarrow \infty$. This is totally a new result which is obtained here.

(iii) The first pressure derivative $(\partial B_T(P, T)/\partial P)_T$ of the bulk modulus decreases with increasing pressure and therefore the second derivative of $B_T(P, T)$ is negative.

(iv) Under the condition that Z is very small, equation (4) can be easily transformed to the well known equation of Murnaghan (1949, 1951).

(v) It is interesting that equation (1) has a general form which is given as

$$[\partial^n B_T(P, T)/\partial P^n]_T / [\partial B_T(P, T)/\partial P]_T = (-1)^{n-1} Z^{n-1} \quad (5)$$

where n is the order of derivative.

The first three results are the same as obtained from the experiments (Spetzler *et al* 1972). Result (iv) suggests that the Murnaghan equation is a special case of the present equation of state. Result (v) suggests that the higher pressure derivative of bulk modulus can be obtained easily once the value of Z and $[\partial B_T(P, T)/\partial P]_T$ become known.

Further, to minimise the adjustable parameters and to have a wide range applicability of the present equation of state, we assume the following.

(a) $B'_T(0, T)$ and Z are temperature-independent quantities, i.e.

$$(\partial B'_T/\partial T)_P = 0 \quad (6a)$$

and

$$(\partial Z/\partial T)_P = 0. \quad (6b)$$

(b) The bulk modulus is a linear function of temperature, i.e.

$$B_T(0, T) = B_T(0, T_0) - (\partial B_T/\partial T)_0(T - T_0). \quad (7)$$

In equations (6) and (7), T_0 is some reference temperature at which $B_T(0, T_0)$ is

known and $(\partial B_T/\partial T)_0$ is the temperature derivative of the bulk modulus at $P = 0$. Putting equations (6) and (7) into equation (3), we get

$$B_T(P, T) = [B_T(0, T_0) - (\partial B_T/\partial T)_0(T - T_0)] + [B'_T(0, T)/Z][1 - \exp(-ZP)]. \quad (8)$$

Further, to compare the results of $V(P, T)/V(0, T)$ obtained from the proposed equation of state with other equations, we use the following equations:

$$V(P, T)/V(0, T) = 1 - a[1 - (1 + bP)^{-c}] \quad (9)$$

and

$$V(P, T)/V(0, T) = [1 - a' \ln(1 + b'P)]^{c'} \quad (10)$$

where

$$a = (1 + B'_0)/(1 + B'_0 + B_0B''_0)$$

$$b = B'_0/B_0 - B''_0/(1 + B'_0)$$

$$c = (1 + B'_0 + B_0B''_0)/(B_0'^2 + B'_0 - B_0B''_0)$$

$$a' = [(B_0'^2 - 4B_0B''_0)^{1/2}]/[(B_0'^2 - 4B_0B''_0)^{1/2} + B'_0]$$

$$b' = [(B_0'^2 - 4B_0B''_0)^{1/2} + B'_0]/2B_0$$

$$c' = 2/[(B_0'^2 - 4B_0B''_0)^{1/2} + B'_0]$$

$$B_0 = B_T(0, T) \quad B'_0 = B'_T(0, T) \quad B''_0 = B''_T(0, T).$$

Equation (9) is given by Huang and Chow (1974) while equation (10) is given by Freund and Ingalls (1989).

We are using these equations for comparison because they are useful for higher-pressure EXAFS work in which one has to express r/r_0 as a function of pressure which is just the third root of $V(P, T)/V(0, T)$ in equations (4), (9) and (10). Here r is the distance between two atoms, e.g. the nearest neighbours.

3. Calculations and results

Thus the volume, bulk modulus and its pressure derivative and other thermodynamic properties can be easily calculated once the four adjustable parameters $B_T(0, T_0)$, $B'_T(0, T_0)$, Z and $(\partial B_T/\partial T)_0$ become known. The three parameters $B_T(0, T_0)$, $B'_T(0, T_0)$ and Z become known once Decker's (1971) compression data at $T_0 = 25^\circ\text{C}$ are fitted with equations (4), (9) and (10). The values of $B_T(0, T_0)$, $B'_T(0, T_0)$ and Z along with the root mean square deviations are reported in table 1. Thus, it is clear from table 1 that the proposed equation of state is better than the other two equations of state used here.

Further, the values of $(\partial B_T/\partial T)_0$ are obtained by fitting the compression data at other temperatures in the case of proposed equation of state. The values of the parameter so obtained are also reported in table 1.

3.1. Compression studies

By making use of equation (4) and taking the values of the parameters from table 1, the values of $V(P, T)/V(0, T)$ are calculated as a function of pressure at different temperatures. For comparison, the calculated and Decker's values are reported in tables 2 and 3 at 25°C for sodium chloride and caesium chloride, respectively. At other

Table 1. Input data used.

Equation used	Solid	T_0 (K)	$B_T(0, T_0)$ (kbar)	$B_T'(0, T_0)$ (kbar)	$Z \times 10^3$ (kbar ⁻¹)	RMS deviation (10 ⁻⁴)	$(\partial B_T / \partial T)_0 \times 10^2$ (kbar K ⁻¹)	$\alpha(0, T_0) \times 10^4$ (K ⁻¹)
Equation (4)	NaCl	298	240.14	4.54	1.236	1.56	12.37	1.1752
Proposed equation	CsCl	298	172.51	4.96	1.306	3.79	11.24	—
Equation (9)	NaCl	298	239.98	4.721	2.872	2.44	—	—
(Proposed equation)	CsCl	298	170.72	5.283	4.217	5.22	—	—
Equation (10)	NaCl	298	239.19	4.745	3.140	2.15	—	—
(Proposed equation)	CsCl	298	170.44	5.322	4.660	4.30	—	—

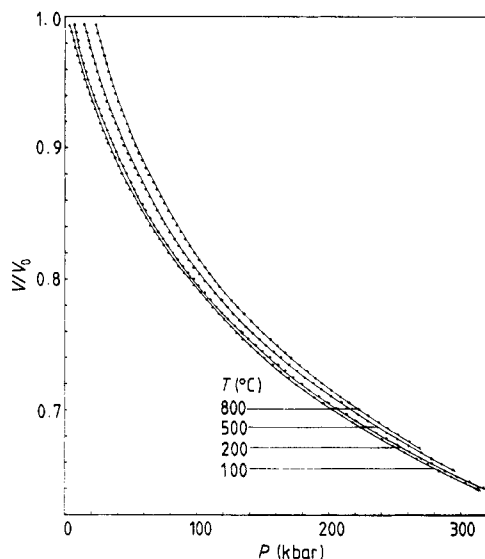


Figure 1. Variation in $V(P, T)/V(0, T)$ with pressure for NaCl at different temperatures: —, calculated; . . . , Decker's data.

temperatures, a comparison is shown in figures 1 and 2. For the whole range of pressures and temperatures, the agreement is very good, particularly where the uncertainties in Decker's results which is 1.1% below 50 kbar, 1.7% below 100 kbar and 2.4% below 200 kbar are taken into account.

Further, it is appropriate to mention here that the accuracies of Decker's results are comparable with the experimental capability. To validate this statement, we calculate $V(P, T)/V(0, T)$ at 25 °C for sodium chloride from the proposed equation of state taking the values of the parameters from table 1 at the pressures used by Liu *et al* (1970). The calculated and the experimental results are reported in table 4. The agreement is very good which indicates the correctness of the statement. The error in volume data of Liu *et al* (1970) is $\pm 0.45\%$.

3.2. Bulk modulus and its first pressure derivative

The isothermal bulk modulus and its first pressure derivative can be easily obtained with the help of equations (3) and (2), respectively, by making use of the parameters from table 1.

The calculated values of $B_T(P, T)$ as a function of pressure at different temperatures for both the solids are reported in figures 3 and 4. However, the variation in $B'_T(P, T)$ as a function of pressure at 25 °C is reported in figure 5. It is clear from figures 3 and 4 that $B_T(P, T)$ does not increase linearly with pressure as is assumed in case of the Murnaghan (1949, 1951) equation.

However, the curves in figures 3 and 4 appear to indicate that it is possible to divide these curves into segments in which $B_T(P, T)$ varies linearly with pressure. A similar conclusion can also be drawn for $B'_T(P, T)$.

It will be interesting to compare calculated values of $B_T(P, T)$ with the experimental data. For this purpose, we report the calculated and the experimental data (Spetzler *et al* 1972) on $B_T(P, T)$ for sodium chloride in the pressure range 0–30 kbar at 300 K in table 5. The agreement is good. However, it may be mentioned here that the calculated values of $B_T(P, T)$ at 550 and 800 K are found to be higher than the experimental values (Spetzler *et al* 1972).

Table 2. $V(P, T)/V(0, T)$ as a function of pressure for sodium chloride at 25 °C.

Sample No.	P (kbar)	$V(P, T)/V(0, T)$		Sample No.	P (kbar)	$V(P, T)/V(0, T)$	
		Decker's data	Calculated			Decker's data	Calculated
1	1.44	0.9940	0.9941	36	91.89	0.7992	0.7990
2	2.94	0.9980	0.9881	37	96.04	0.7940	0.7939
3	4.47	0.9821	0.9823	38	100.31	0.7889	0.7888
4	6.06	0.9762	0.9764	39	104.69	0.7838	0.7837
5	7.70	0.9703	0.9705	40	109.21	0.7787	0.7786
6	9.38	0.9644	0.9648	41	113.84	0.7736	0.7736
7	11.12	0.9586	0.9588	42	118.61	0.7686	0.7685
8	12.91	0.9528	0.9530	43	123.52	0.7636	0.7635
9	14.76	0.9470	0.9472	44	128.55	0.7586	0.7586
10	16.67	0.9412	0.9414	45	133.73	0.7536	0.7536
11	18.63	0.9354	0.9356	46	139.06	0.7486	0.7487
12	20.65	0.9297	0.9299	47	144.53	0.7437	0.7437
13	22.74	0.9240	0.9241	48	150.15	0.7388	0.7387
14	24.88	0.9183	0.9185	49	155.93	0.7339	0.7340
15	27.10	0.9127	0.9128	50	161.87	0.7290	0.7291
16	29.37	0.9070	0.9071	51	167.97	0.7242	0.7243
17	31.72	0.9014	0.9015	52	174.25	0.7193	0.7195
18	34.13	0.8958	0.8959	53	180.69	0.7145	0.7147
19	36.62	0.8903	0.8903	54	187.31	0.7097	0.7099
20	39.18	0.8847	0.8847	55	194.12	0.7050	0.7051
21	41.82	0.8792	0.8791	56	201.11	0.7002	0.7004
22	44.53	0.8737	0.8736	57	208.29	0.6955	0.6957
23	47.32	0.8683	0.8682	58	215.67	0.6908	0.6910
24	50.20	0.8628	0.8627	59	223.26	0.6861	0.6863
25	53.16	0.8574	0.8572	60	231.05	0.6815	0.6816
26	56.20	0.8520	0.8518	61	239.05	0.6768	0.6769
27	59.33	0.8466	0.8464	62	247.27	0.6722	0.6723
28	62.55	0.8412	0.8411	63	255.72	0.6676	0.6677
29	65.87	0.8359	0.8357	64	264.39	0.6631	0.6631
30	69.28	0.8306	0.8304	65	273.31	0.6585	0.6584
31	72.79	0.8253	0.8251	66	282.46	0.6540	0.6539
32	76.40	0.8200	0.8198	67	291.87	0.6495	0.6493
33	80.11	0.8148	0.8146	68	301.53	0.6450	0.6447
34	83.93	0.8096	0.8094	69	311.45	0.6405	0.6401
35	87.85	0.8044	0.8042				

3.3. Thermal coefficient

It will be really interesting to study the coefficient of thermal expansion as a function of pressure. For this purpose we use the idea given by Dass and Kumari (1984). They have pointed out that the product of the measured isothermal bulk modulus $B_T(P, T)$ and the thermal expansion coefficient $\alpha(P, T)$, is approximately independent of pressure:

$$\alpha(P, T)B_T(P, T) = \alpha(0, T)B_T(0, T) = \varepsilon(T). \quad (11)$$

Equation (11) has also been shown to be valid at least to a good approximation by Swenson (1968), Yagi (1978) and Boehler and Kennedy (1980a). Putting the value of $B_T(P, T)$ from equation (3) into equation (11), we get

$$\alpha(P, T) = \alpha(0, T)\{1 + (B'_T(0, T)/B_T(0, T)Z)[1 - \exp(-ZP)]\}^{-1}. \quad (12)$$

Thus, equation (12) can be used to determine $\alpha(P, T)$ as a function of pressure.

Table 3. $V(P, T)/V(0, T)$ as a function of pressure for caesium chloride at 25 °C.

No.	P (kbar)	$V(P, T)/V(0, T)$		No.	P (kbar)	$V(P, T)/V(0, T)$	
		Decker's data	Calculated			Decker's data	Calculated
1	2.08	0.9880	0.9883	22	99.71	0.7586	0.7582
2	4.32	0.9762	0.9767	23	108.29	0.7486	0.7483
3	6.72	0.9644	0.9650	24	117.40	0.7388	0.7386
4	9.29	0.9528	0.9534	25	127.07	0.7290	0.7289
5	12.04	0.9412	0.9418	26	137.33	0.7193	0.7193
6	14.98	0.9297	0.9303	27	148.21	0.7097	0.7098
7	18.13	0.9183	0.9188	28	159.76	0.7002	0.7004
8	21.49	0.9070	0.9074	29	172.00	0.6908	0.6910
9	25.08	0.8958	0.8961	30	184.98	0.6815	0.6818
10	28.91	0.8847	0.8849	31	198.73	0.6722	0.6726
11	33.00	0.8737	0.8737	32	213.31	0.6631	0.6635
12	37.36	0.8628	0.8627	33	228.76	0.6540	0.6544
13	42.00	0.8520	0.8518	34	245.13	0.6450	0.6454
14	46.95	0.8412	0.8409	35	262.47	0.6361	0.6365
15	52.91	0.8306	0.8302	36	280.83	0.6272	0.6276
16	57.81	0.8200	0.8196	37	300.28	0.6185	0.6188
17	63.77	0.8096	0.8091	38	320.88	0.6098	0.6100
18	70.11	0.7992	0.7987	39	342.68	0.6012	0.6012
19	76.85	0.7889	0.7884	40	365.77	0.5927	0.5925
20	84.01	0.7787	0.7783	41	390.20	0.5843	0.5834
21	91.62	0.7686	0.7682	42	416.06	0.5759	0.5751

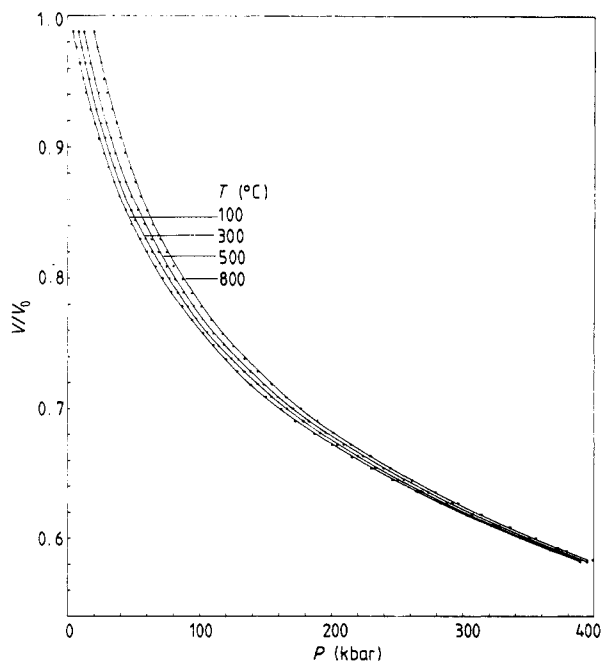
**Figure 2.** Variation in $V(P, T)/V(0, T)$ with pressure for CsCl at different temperatures: —, calculated; ····, Decker's data.

Table 4. $V(P, T)/V(0, T)$ as a function of pressure at 25 °C for sodium chloride. The experimental data are taken from Liu *et al* (1970).

P (kbar)	$V(P, T)/V(0, T)$	
	Experimental	Calculated
40	0.883	0.8829
78	0.819	0.8175
84	0.810	0.8093
95	0.796	0.7951
102	0.788	0.7868
110	0.778	0.7777
137	0.751	0.7505
161	0.731	0.7298
170	0.722	0.7227
183	0.713	0.7130
190	0.708	0.7080
194	0.705	0.7052
200	0.701	0.7011
202	0.699	0.6998
204	0.698	0.6985
222	0.687	0.6870
232	0.680	0.6810
235	0.679	0.6793
247	0.672	0.6724
268	0.660	0.6611
272	0.658	0.6591
288	0.650	0.6511
290	0.649	0.6501
300	0.645	0.6454

The calculations of $\alpha(P, T)$ are carried out for sodium chloride at 300 K in order to compare them with the available experimental data for this solid.

$\alpha(P, T)$ is calculated with the help of equation (12) and taking the values of parameters needed from table 1. The calculated and the experimental values are reported

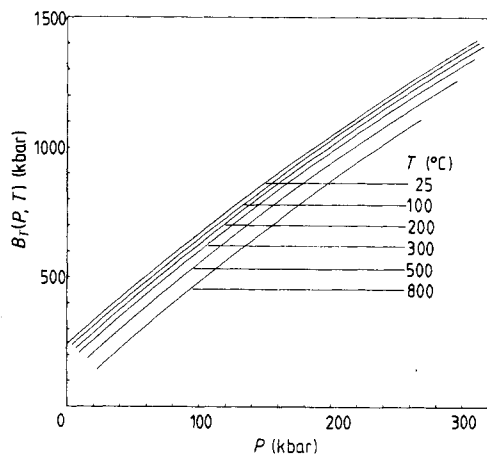


Figure 3. Variation in $B_T(P, T)$ with pressure for NaCl at different temperatures.

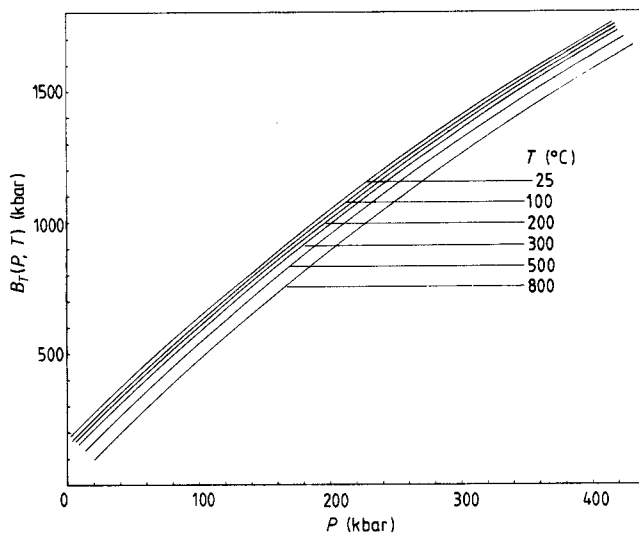


Figure 4. Variation in $B_T(P, T)$ with pressure for CsCl at different temperatures.

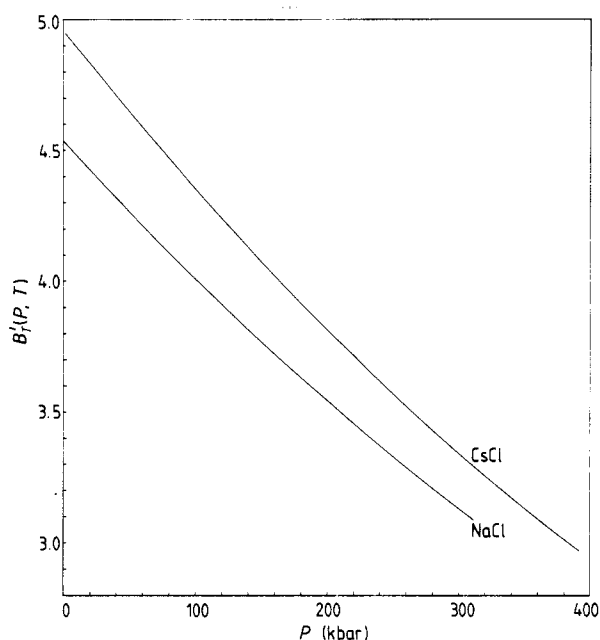


Figure 5. Variation in $B'_T(P, T)$ with pressure for NaCl and CsCl at 25 °C.

in table 5. The experimental values in parentheses are taken from Boehler and Kennedy (1980b).

Our calculated values of $\alpha(P, T)$ are closer to the values reported by Boehler and Kennedy (1980b) than to the values given by Spetzler *et al* (1972). Even then, the agreement between the calculated and the experimental values is good.

Table 5. $B_T(P, T)$ and $\alpha(P, T)$ as a function of pressure at 300 K for sodium chloride. The experimental data are taken from Spetzler *et al* (1972) and the experimental values in parentheses are taken from Boehler and Kennedy (1980b).

P (kbar)	$B_T(P, T)$ (kbar)		$\alpha(P, T) \times 10^{-4}$ (K)	
	Calculated	Experimental	Calculated	Experimental
0	240.14	238.41	1.1752	1.1752 (1.169)
2	249.21	248.96	1.1324	1.1218
4	258.25	259.17	1.0928	1.0737
5	262.77	—	1.074	(1.054)
6	267.28	269.02	1.0559	1.0299
8	276.28	278.49	1.0215	0.9899
10	285.26	287.55	0.9893	0.9532 (0.968)
15	307.61	—	0.917	(0.898)
20	329.83	—	0.856	(0.841)
25	351.90	—	0.802	(0.796)
30	373.84	—	0.756	(0.756)

Thus, equation (12) can also be used at high pressures and various temperatures to calculate $\alpha(P, T)$ once the values of $B_T(P, T)$ become known as a function of pressure and temperature. It may be mentioned here that the calculated values of $\alpha(P, T)$ at 550 and 800 K in the pressure range 0–10 kbar are found to be in agreement with the experimental data (Spetzler *et al* 1972).

3.4. The Anderson–Grüneisen parameter

The physical significance of the Anderson–Grüneisen parameter δ_T has been emphasised by several workers (Anderson 1966, 1967, Chang 1967, Broadhurst and Mopsik 1970, Dass and Kumari 1984).

The parameter is defined as

$$\delta_T(P, T) = - \{1/[\alpha(P, T)B_T(P, T)]\}[\partial B_T(P, T)/\partial T]_P. \quad (13)$$

On the basis of the Grüneisen relation, Chang (1967) expressed δ_T as

$$\delta_T(P, T) = [\partial B_T(P, T)/\partial P]_T - 1 \quad (14)$$

whereas Dass and Kumari (1984) expressed this parameter as

$$\delta_T(P, T) = [\partial B_T(P, T)/\partial P]_T. \quad (15)$$

Equations (14) and (15) are derived on the assumptions that $q = 0$ and $q = 1$, respectively, and also that C_V is independent of pressure; here q is the second Grüneisen parameter and is defined in term of Grüneisen parameter $\gamma = \alpha V B_T / C_V$ as

$$q = [\partial \ln \gamma / \partial \ln V]_T. \quad (16)$$

It is appropriate to mention here that equation (15) is certainly better than equation (14) on the grounds that Boehler (1983) have found the value of $q \approx 1.0$ experimentally. Thus the value of and the variation in $\delta_T(P, T)$ with pressure are the same as those for $B_T(P, T)$ as reported in figure 5.

4. Conclusion

It can be concluded from the discussion given above that the present equation of state is quite successful in representing $V(P, T)/V(0, T)$ behaviour at high pressures and high

temperatures. However, it may be mentioned here that the present results will definitely improve further if the temperature variation of $B_T'(P, T)$ is also taken into the theory. This will also remove the drawback of the theory that $\delta_T(P, T)$ is a temperature-independent quantity although the adjustable parameters will increase from four to five.

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References

- Anderson O L 1966 *Phys. Rev.* **144** 553
— 1967 *J. Geophys. Res.* **72** 3661
Birch F 1952 *J. Geophys. Res.* **57** 227
Boehler R 1983 *Phys. Rev. B* **27** 6754
Boehler R and Kennedy G C 1980a *J. Phys. Chem. Solids* **41** 1019
— 1980b *J. Phys. Chem. Solids* **41** 517
Broadhurst M G and Mopsik I I 1970 *J. Chem. Phys.* **52** 3634
Chang Y A 1967 *J. Phys. Chem. Solids* **28** 697
Dass N and Kumari M 1984 *Phys. Status Solidi b* **124** 531
Decker D L 1971 *J. Appl. Phys.* **42** 3239
Freund J and Ingalls R 1989 *J. Phys. Chem. Solids* **51** 263
Huang Y K and Chow C Y 1974 *J. Phys. D: Appl. Phys.* **7** 2021
Keane A 1954 *Aust. J. Phys.* **7** 323
Liu Lin-Gun, Takahashi T and Bassett W A 1970 *J. Phys. Chem. Solids* **31** 1345
Murnaghan F D 1949 *Proc. Symp. Appl. Math.* **1** 158
— 1951 *Finite Deformation of an Elastic Solid* (New York: Wiley) ch 4
Spetzler H, Sammis C G and O'Connell R J 1972 *J. Phys. Chem. Solids* **33** 1727
Swenson C 1968 *J. Phys. Chem. Solids* **29** 1337
Yagi T 1978 *J. Phys. Chem. Solids* **39** 563