

Pressure dependence of thermodynamic properties of NaBr, NaI and AgCl

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Abstract. Various state-equations, derived by expanding energy as a function of volume in Taylor series and using different order Pade's approximants, have been combined with quasi-harmonic approximation for free energy to reproduce the pressure dependence of thermodynamic properties of NaBr, NaI and AgCl crystals. We have used these state-equations to compute the reduced volume, the isothermal bulk modulus and the pressure derivative of isothermal bulk modulus for the three crystals at various pressures (up to 80 kbar) and at room temperature ($T = 298$ K). The results obtained are reasonably good lending support to the state-equations and the technique used to extend their applicability. The significant results obtained in the present study include the unified reduced equation of state for the three crystals which generates almost a single curve for the $P - V$ behaviour at room temperature.

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1. Introduction

The determination of the pressure dependence of thermodynamic properties that characterize a solid is a problem of considerable importance to high-pressure physics and geophysics.

In principle, all of the thermodynamic properties of a system can be predicted once the form of the interatomic forces is known. However since our knowledge of these forces is incomplete and our ability to carry through the prediction procedure is limited, simplified models and approximations are needed.

Our interest here is in the prediction of the high pressure properties of NaBr, NaI and AgCl crystals with the aid of various state-equations and the interionic force model.

In our earlier paper (Thakur and Dwary 1986), we have studied the pressure dependence of thermodynamic properties of NaCl crystal with the use of $f^{(0)}$, $f^{(1)}$ and $f^{(2)}$ involved in the expression for Helmholtz free energy per unit cell in the quasi-harmonic approximation. Keeping in view the unavailability of these three quantities for other crystals, we modify our method of calculation in the present paper. Here, we have computed the pressure dependence of thermodynamic properties of the three crystals with careful use of B_0 (the isothermal bulk modulus at zero pressure) and B'_0 (the pressure derivative of isothermal bulk modulus at zero pressure).

The results obtained are in good agreement with the experimental results over a wide range of pressure up to 80 kbar.

2. Theory

In our present study we use the same state-equations referred to as laws A, B, C, D and E, as used in our previous paper (Thakur and Dwary 1986)

$$P_B = x/(1 - x) \quad (1)$$

$$P_B = x + x^2/(1 - \gamma x) \quad (2)$$

$$P_B = x + x^2[1 - \ln(1 - \gamma x)] \quad (3)$$

$$P_B = x + x^2 \exp(\gamma x) \quad (4)$$

$$P_B = x + x^2(1 + \gamma x) \quad (5)$$

where

$$P_B = P/\alpha \quad \text{and} \quad x = (V_0 - V)/\beta$$

P is the external hydrostatic pressures, V the volume at pressure P , $V_0 = V$ at $P = 0$, α and β are the characteristic parameters of the crystal, known as internal pressure and free volume respectively and γ is a dimensionless parameter.

The above expression for x generates the following expression for the reduced volume

$$\frac{V}{V_0} = (1 - \beta_1 x) \quad (6)$$

where $\beta_1 (= \beta/V_0)$ is a dimensionless quantity. The expression for isothermal bulk modulus $B = -V(dp/dV)_T$ from first principles, when combined with (6) generates the following expressions for isothermal bulk modulus and its pressure derivative.

$$B = \left(\frac{1 - \beta_1 x}{\beta_1} \right) \alpha \cdot P_B^1 \quad (7)$$

$$\frac{dB}{dP} = \left(\frac{1 - \beta_1 x}{\beta_1} \right) \frac{P_B''}{P_B'} - 1 \quad (8)$$

where $P_B' = dP_B/dx$ and $P_B'' = d^2 P_B/dx^2$.

3. Determination of the coefficients α , β_1 and γ

Using the facts that at $P = 0$, $P_B' = 1$ and $P_B'' = 2$, eqs (7) and (8) generate the following expressions

$$\alpha = \beta_1 \cdot B_0 \quad (9)$$

$$\beta_1 = 2/(1 + B_0'). \quad (10)$$

In our earlier paper (Thakur and Dwary 1986) we have used the following expressions

$$\gamma = g_1''(26g_1'' - 6g_1''' + \frac{1}{2}g_1'''')/27(g_1'' - g_1'''/6)^2 \quad (11)$$

$$g_1'' = 9/K_1^0 = 9B_0/P_r \quad (12)$$

and

$$\beta_1 = g_1''/(g_1'' - g_1'''/6)$$

or

$$g_1''' = 6g_1''(1 - 1/\beta_1) \quad (13)$$

where $P_r (= E_0/K_s a_0^3)$ is the reference pressure, E_0 the lattice energy, a_0 the equilibrium interatomic distance and K_s the structure parameter of the crystal ($K_s = 2$ for NaCl-structure, $K_s = 1.54$ for CsCl-structure).

The expression for the reduced energy $E_1 (= -E/E_0)$ as derived in our earlier paper (Thakur and Dwary 1986) gives the following expressions after neglecting $f^{(2)}(a_1 - 1)^2/2$ term

$$E_1 = \frac{-C_1/a_1 + (\rho_1 C_1 + \rho_1 f^{(1)}) \exp[(1 - a_1)/\rho_1] + f^{(0)} + f^{(1)}(a_1 - 1)}{C_1 - C_1 \rho_1 - f^{(1)} \rho_1 - f^{(0)}} \quad (14)$$

$$\rho_1 = (2C_1 + g_1'' E_0)/(6C_1 - g_1''' E_0) \quad (15)$$

and

$$g_1'''' = \left[\frac{d^4 E_1}{da_1^4} \right]_{a_1=1} = [-24C_1 + (2C_1 + g_1'' E_0)/\rho_1^2]/E_0. \quad (16)$$

where $C_1 = Ae^2/a_0$, A is the Madelung's constant of the crystal.

The present method of calculation, thus enables us to determine the coefficients α , β_1 and γ if the values of B_0 and B_0' together with the input parameters a_0 , $E_0 A$ and K_s are known.

The experimental values of the input parameters, which form the basis of the theory are collected in table 1, which are from Thakur (1982), Woodcock (1974) and Spetzler *et al* (1972).

The values of B_0 and B_0' together with $B_0'' (= d^2 B/dp^2, \text{ at } P=0)$ are evaluated by fitting modified Murnaghan equation (taken from Vaidya and Kennedy 1971)

$$\frac{V}{V_0} = \left(\frac{2B_0 + B_0' P - A_0 P}{2B_0 + B_0' P + A_0 P} \right)^{1/A_0} \quad (17)$$

With

$$A_0 = (B_0'^2 - 2B_0 B_0'')^{1/2}$$

Table 1. Model parameters for NaBr, NaI and AgCl (at 298 K).

	NaBr	NaI	AgCl
$a_0(A)$	2.989	3.237	2.772
$E_0(\text{kJ mol}^{-1})$	736.0	695.8	900.57
A	1.74756	1.74756	1.74756
K_s	2	2	2

Table 2. Compressibility parameters for NaBr, NaI and AgCl (at 298 K).

	NaBr	NaI	AgCl
B_0 (kbar)	194	152	460
B'_0	5.3	4.6	2.4
B''_0 (kbar ⁻¹)	-0.0299	-0.02632	-0.00452

Table 3. Parameters of the state-equations derived for NaBr, NaI and AgCl (at 298 K).

	NaBr	NaI	AgCl
α (kbar)	61.5873	54.2857	270.5882
β_1	0.3174603	0.3571428	0.5882353
γ	0.6559154	0.6721572	0.7647162

to the experimental data of V/V_0 by Bridgman (1945). The evaluated values of B_0 , B'_0 and B''_0 are listed in table 2.

The parameters of the state-equation α , β_1 and γ obtained from (9), (10) and (11) respectively, are collected in table 3.

4. Calculation and results

In order to study the pressure dependence of thermodynamic properties of NaBr, NaI and AgCl crystals, we first, compute the values of x corresponding to various pressures (up to 80 kbar) according to laws A, B, D and E. Law C is not presented here as it gives almost the same result as obtained from Law D. However one can obtain the complete results according to laws A to E from the authors. The results obtained are listed in table 4 which form the basis of the present computation. Once the values of x as a function of pressure are known, the corresponding values of the reduced volume, the isothermal bulk modulus and its pressure derivative can readily be obtained for realistic comparison with the experimental data.

4.1 Reduced volume

Various static and dynamic methods have been used so far in order to measure the reduced volume (V/V_0) for different metal halides by several investigators, Slater (1924); Bridgman (1940, 1945); Drickamer *et al* (1966); Schock and Jamieson (1969) and Vaidya and Kennedy (1971). Here, we compute theoretically the reduced volume for the three crystals at various pressures (up to 80 kbar) from (6).

The computed values of the reduced volume (V/V_0) have been plotted as a function of pressure at room temperature ($T = 298$ K) in figure 1 for laws A, B, D and E. Figure 1 also contains the experimental points obtained from Bridgman (1945).

Table 4. Calculated values of $x(= (V_0 - V)/\beta)$ for NaBr, NaI and AgCl (at 298 K) according to laws A, B, D and E, which form the basis of present computation.

<i>P</i> (kbar)	Laws	NaBr	NaI	AgCl
1	2	3	4	5
5	A	0.07509	0.08434	0.01814
	B	0.07523	0.08453	0.01814
	D	0.07524	0.08454	0.01814
	E	0.07524	0.08455	0.01814
10	A	0.13969	0.15556	0.03564
	B	0.14060	0.15675	0.03565
	D	0.14067	0.15687	0.03565
	E	0.14074	0.15697	0.03565
15	A	0.19585	0.21649	0.05252
	B	0.19834	0.21969	0.05256
	D	0.19862	0.22013	0.05256
	E	0.19885	0.22049	0.05256
20	A	0.24514	0.26923	0.06883
	B	0.24999	0.27537	0.06890
	D	0.25067	0.27642	0.06891
	E	0.25123	0.27724	0.06891
25	A	0.28873	0.31531	0.08458
	B	0.29666	0.32519	0.08472
	D	0.29797	0.32716	0.08473
	E	0.29900	0.32865	0.08474
30	A	0.32756	0.35593	0.09980
	B	0.33917	0.37019	0.10003
	D	0.34135	0.37341	0.10006
	E	0.34300	0.37577	0.10009
35	A	0.36237	0.39200	0.11453
	B	0.37814	0.41114	0.11488
	D	0.38144	0.41593	0.11493
	E	0.38386	0.41933	0.11497
40	A	0.39375	0.42424	0.12879
	B	0.41408	0.44865	0.12928
	D	0.41873	0.45531	0.12935
	E	0.42205	0.45992	0.12942
45	A	0.42219	0.45324	0.14259
	B	0.44739	0.48318	0.14326
	D	0.45361	0.49200	0.14337
	E	0.45795	0.49797	0.14346
50	A	0.44808	0.47945	0.15596
	B	0.47837	0.51514	0.15683
	D	0.48638	0.52637	0.15699
	E	0.49187	0.53383	0.15713
55	A	0.47175	0.50327	0.16892
	B	0.50732	0.54482	0.17003
	D	0.51731	0.55872	0.17025
	E	0.52404	0.56777	0.17043

(Continued)

Table 4. (Continued)

P(kbar)	Laws	NaBr	NaI	AgCl
1	2	3	4	5
60	A	0.49347	0.52500	0.18149
	B	0.53444	0.57250	0.18286
	D	0.54661	0.58927	0.18315
	E	0.55466	0.60003	0.18339
65	A	0.51348	0.54491	0.19369
	B	0.55992	0.59839	0.19535
	D	0.57444	0.61824	0.19572
	E	0.58390	0.63078	0.19603
70	A	0.53197	0.56322	0.20553
	B	0.58394	0.62267	0.20751
	D	0.60096	0.64578	0.20798
	E	0.61190	0.66020	0.20836
75	A	0.54910	0.58011	0.21702
	B	0.60662	0.64552	0.21936
	D	0.62629	0.67204	0.21994
	E	0.63878	0.68840	0.22041
80	A	0.56502	0.59574	0.22819
	B	0.62809	0.66706	0.23090
	D	0.65054	0.69715	0.23161
	E	0.66464	0.71551	0.23218

4.2 Isothermal bulk modulus

The pressure dependence of compressibility coefficient has been determined empirically (Lister 1974) and semi-empirically (Huang and Chow 1974; Huang 1975, 1977). These methods use the bulk modulus and its pressure derivatives in different pressure-ranges as input data. Here, we compute the isothermal bulk modulus for the three crystals at various pressures (up to 80 kbar) from (7).

The computed values of the isothermal bulk modulus (B) have been plotted as a function of pressure at room temperature ($T = 298$ K) in figure 2 for laws A, B, D and E. Figure 2 also contains the points obtained from equation

$$B = B_0 + B'_0 P + \frac{1}{2} B''_0 P^2 \quad (18)$$

which is the basis of the modified Murnaghan equation (17).

4.3 Pressure derivative of bulk modulus

The pressure derivative of isothermal bulk modulus which is also known as Meolwyn Hughes parameter, plays an important role in the physics of solids (Thakur 1976, 1982). We compute here the values of pressure derivative of isothermal bulk modulus (dB/dP) for three crystals from (8). The computed values have been plotted as a

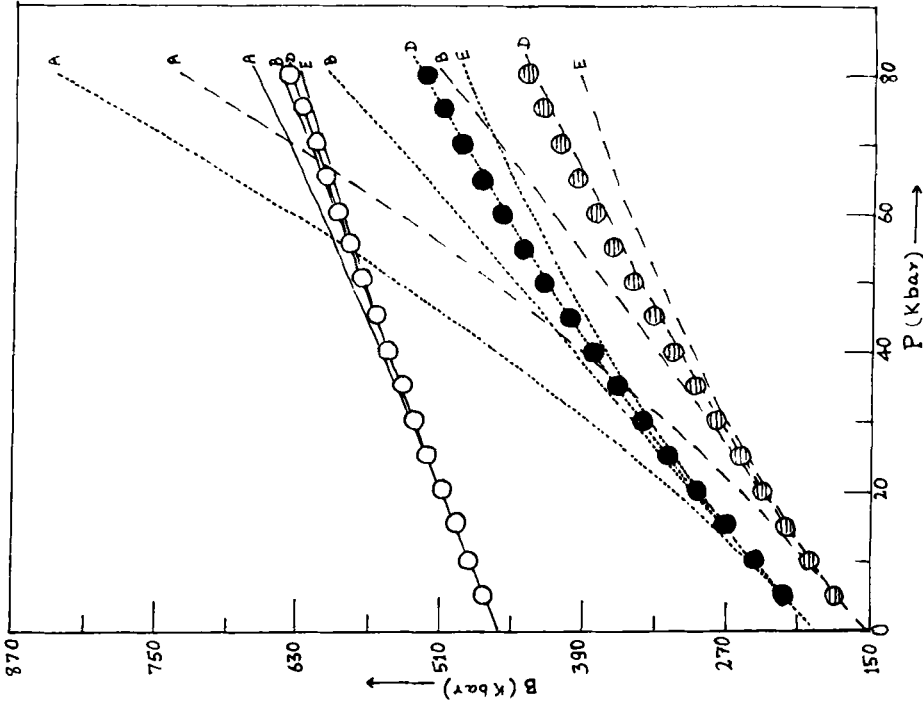


Figure 2. Variation of isothermal bulk modulus (B) with pressure (P) for AgCl (full curve), NaBr (dotted curve) and NaI (broken curve) according to (A) law A, (B) law B, (D) law D and (E) law E at $T = 298$ K, together with the points calculated from (18) (open circles, AgCl, full circles, NaBr and shaded circles, NaI).

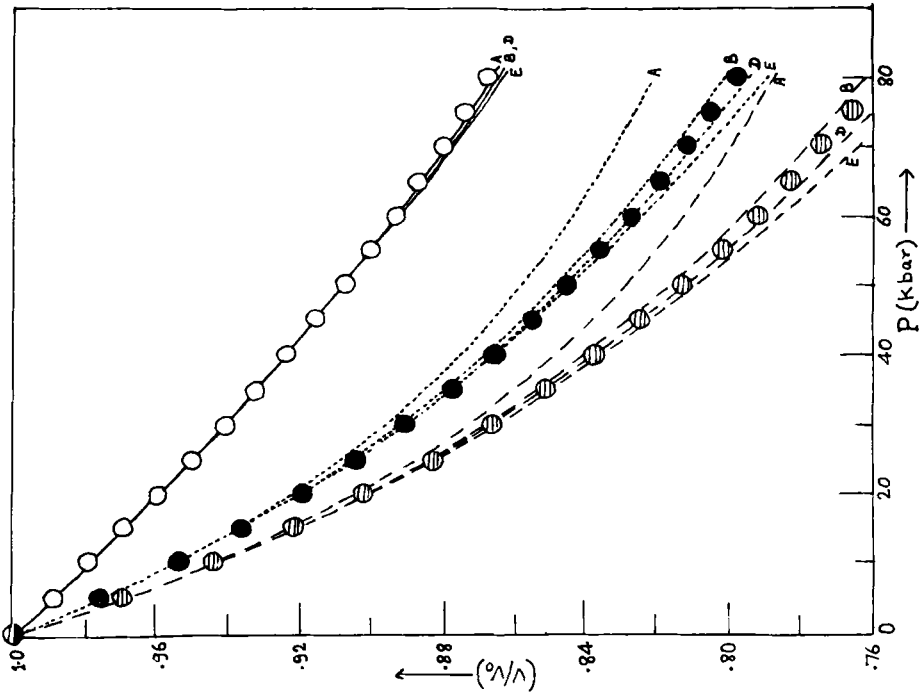


Figure 1. Variation of reduced volume (V/V_0) with pressure (P) for AgCl (full curve), NaBr (dotted curve) and NaI (broken curve) according to (A) law A, (B) law B, (D) law D and (E) law E at $T = 298$ K, together with the experimental points (open circles, AgCl, full circles, NaBr and shaded circles, NaI).

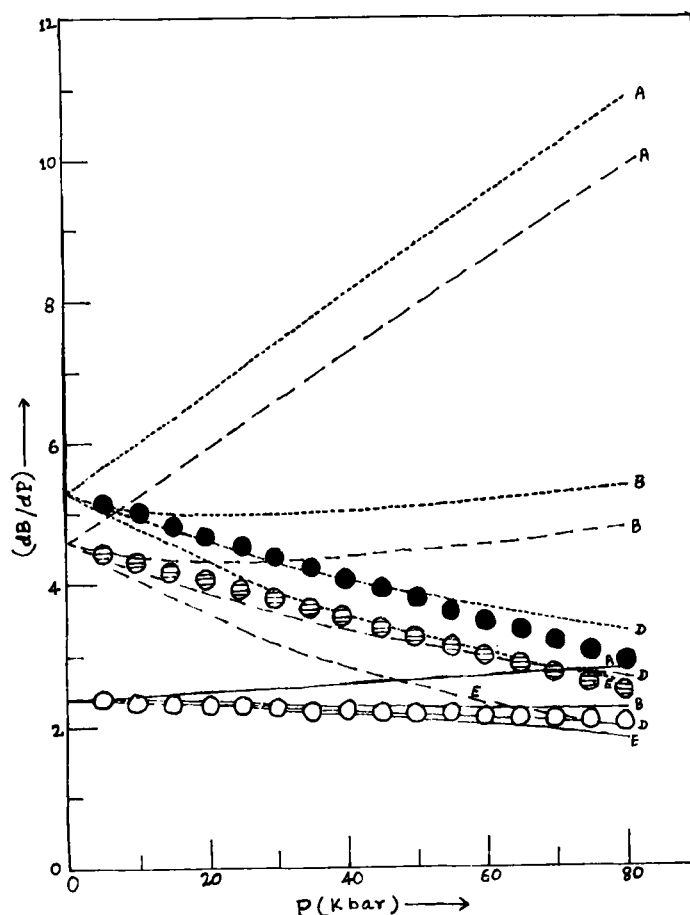


Figure 3. Variation of pressure derivative of bulk modulus (dB/dP) with pressure (P) for AgCl (full curve), NaBr (dotted curve) and NaI (broken curve) according to (A) law A, (B) law B, (D) law D and (E) law E at $T = 298$ K, together with the points calculated from (19) (open circles AgCl, full circles, NaBr and shaded circles, NaI).

function of pressure at room temperature ($T = 298$ K) in figure 3 for laws A, B, D and E. Figure 3 also contains the points obtained from equation

$$\frac{dB}{dP} = B'_0 + B''_0 P \quad (19)$$

which has been derived from (18).

5. Discussion of the results

5.1 Reduced volume

Figure 1 indicates that for AgCl crystal all laws from A to E yield the same result coincident with the experimental points over a wide range of pressure up to 50 kbar. However beyond this pressure law A is slightly deviated from laws B, D and E which

are almost coinciding with each other. In the case of NaBr and NaI crystals, laws A to E all give almost the same result coincident with the experimental points in low pressure range. However at high pressures law D is found quite close to the experimental points, law E shows a small deviation and law B a greater deviation whereas law A tends to move far from the experimental points.

So, as far as the P - V behaviour of the three crystals is concerned, we may classify laws A to E in order of superiority;

$$\text{law D} > \text{law E} > \text{law B} > \text{law A.} \quad (20)$$

Figure 1 also indicates that for each of the three crystals V/V_0 decreases with increasing pressure, the rate of decrease being smaller at higher pressure.

After getting encouraging results for P - V behaviour according to law D, we have plotted the computed values of (V/V_0) as a function of (P/B_0) according to this laws in figure 4. Surprisingly, this plot almost lies on a single curve for each of the three crystals thus showing a good agreement with the experimental results given by Smith

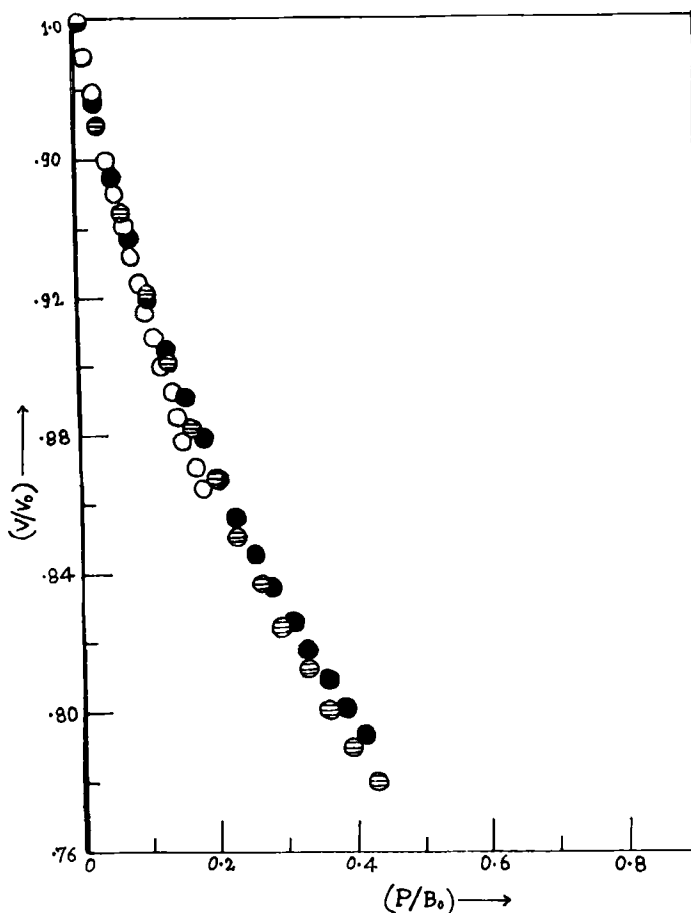


Figure 4. Variation of reduced volume (V/V_0) with (P/B_0) for AgCl (open circles) NaBr (full circles) and NaI (shaded circles) according to law D at $T = 298$ K.

and Mclean (1973), except in high pressure range where we find a slight deviation between the plots for the three crystals.

5.2 Isothermal bulk modulus

Figure 2 indicates that for each of the three crystals, laws B, D and E give almost the same result at low pressures as calculated from (18). However at high pressures law D is found very close to the points calculated from (18), law E is slightly deviated and law B is more deviated whereas law A is highly deviated even in low pressure-range. So on this basis we get the same order of superiority as (20).

Figure 2 also indicates that for each crystal the isothermal bulk modulus (B) increases with increasing pressure. The rate of increase of B with respect to the pressure, decreases for law D and E, remains almost constant for law B and increases for law A, with the increase in pressure.

5.3 Pressure derivative of bulk modulus

Figure 3 indicates that the pressure derivative of isothermal bulk modulus (dB/dP) for each crystal decreases with increasing pressure according to law D and E, the nature of variation being supported by the results obtained from (19). Law B shows the same nature of variation in low pressure range but the opposite nature in high pressure range whereas law A shows the opposite nature throughout the entire range of pressure.

Though, law D shows relatively better agreement with the results obtained by (19), yet there is a small discrepancy between the two results. This discrepancy arises due to the fact that the power series of B , equation (18), used to derive the modified Murnaghan equation (17) extends only up to second power of P which generates a linear variation of (dB/dP) with P as represented by (19). However our theoretical line, according to law D, shows a slight curvature. This discrepancy may be minimized if we extend the power series of B up to third power of P in order to derive the Murnaghan equation in further suitably modified form.

6. Conclusion

A simple expansion of energy as a function of volume in Taylor's series and subsequent approximation of the series by the Pade's approximation, permit the various laws A to E for the calculation of (V/V_0), B and (dB/dP).

Laws A to E were basically developed for the static state-equations (i.e. for $T = 0$). However, the technique developed and used in the present study permits the use of the same state-equation (laws A to E) for describing the behaviour of solids at room temperature as well. The results obtained are encouraging and lend support to the present technique of using laws A to E at the room temperature.

As far as the relative merit of various laws (A to E) is concerned, the present study indicates the superiority of law D over laws A, B and E.

In addition to the findings of reasonable results for the variation of reduced volume, isothermal bulk modulus and pressure derivative of bulk modulus, as a function of pressure, we also find that the plots of (V/V_0) as a function of (P/B_0) for all three crystals, almost lie on a single curve.

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