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HighPressure Equation of State for NaCl, KCl, and CsCl

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High-Pressure Equation of State for NaCl, KCl, and CsCl

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A calculation of the equation of state for NaCl from a Mie-Grüneisen equation was repeated using more accurate values of the zero-pressure compressibility. It was also extended to KCl and CsCl. An analysis of this approach to pressure calibration indicates that it will yield pressures with about the same accuracy as can be presently achieved by experimental measurements above 25 kbar, and thus furnishes a temporary practical pressure scale.

I. INTRODUCTION

A calculation of the equation of state of NaCl [1] (this paper will be referred to as DDI), which was estimated to be accurate to 2% below 150 kbar and 1500 °C, has proven to be very useful as a pressure indicator. Recent measurements, intended as fixed-point calibrations,[2,3] coupled with x-ray measurements of these calibrants vs NaCl compression[4,5] have born out the usefulness of the theory but indicate that the original calculation is about 3% low. Since the original equation-of-state calculations were completed, several accurate measurements of the adiabatic bulk modulus of NaCl at atmospheric pressure have been reported,[6–9] which differ appreciably from the value used in DDI. Since the bulk modulus is one of the important input parameters in this semiempirical calculation, it was felt that it would be worthwhile repeating the calculation using the more accurate input.[10] In addition the equations of state for KCl and CsCl were calculated by exactly the same technique as a check on the validity of the theory. These materials were chosen because one could then calculate the electron affinity for Cl and compare with experiment for another check on the consistency of the approach. CsCl is also interesting in that it is arranged in a different crystal structure from NaCl and has a greatly different ratio of cation to anion radii which is important in the second-nearest-neighbor repulsion terms. It is also a material that remains in a single phase to very high pressures.

PROCEDURE

The calculation was carried out in the same manner as in DDI with one minor modification. We improved the method for determining the variation of the Grüneisen parameter γ with volume and assumed a volume dependence of the form

$$\gamma=\gamma_0(V/V_0)^A, \tag{1}$$

TABLE I. Parameters used in the calculation at 25 °C and atmospheric pressure.

	r_0 (Å)	r_+[a] (Å)	r_-[a] (Å)	θ_0 (°K)	γ_0	$B_s(0)$ (kbar)
NaCl	2.8200 ± 7[b]	1.20 ± 0.06	1.62 ± 0.06	279 ± 11[c]	1.59 ± 0.05[d]	250.3 ± 0.8[e]
KCl	3.1466 ± 15[f]	1.15 ± 0.06	1.64 ± 0.06	236 ± 18[g]	1.48 ± 0.05[d]	182.8 ± 0.7[h]
CsCl	3.5672 ± 5[i]	1.85 ± 0.10	1.72 ± 0.06	151 ± 10[j]	1.99 ± 0.10[k]	181.3 ± 1.1[l]
	C[m]	D[n]	b_+/b	b_-/b[o]	A	$1/\rho$ (Å^{-1})	b (erg)
NaCl	1.40 ± 0.1	1.8 ± 0.6	6.33 ± 2.2	0.54 ± 0.01	$0.93^{+.37}_{-.23}$	3.2038	2.1068×10^{-9}
KCl	4.38 ± 0.4	5.6 ± 1.9	1.74 ± 0.6	0.70 ± 0.06	$1.04^{+.46}_{-.24}$	3.1163	4.3506×10^{-9}
CsCl	25.1 ± 3	26 ± 9	0.97 ± 0.2	1.03 ± 0.15	$1.18^{+.52}_{-.28}$	2.8943	5.6102×10^{-9}

[a] M.P. Tosi and F.G. Fumi, J. Phys. Chem. Solids **25**, 31, (1964); **25**, 45 (1964).
[b] Natl. Bur. Std. Circular No. 539, (U.S. GPO, Washington, D.C., 1953), Vol. 2, pp. 41 and 44.
[c] Reference 18. Also T.H.K. Barron, W.T. Berg, and J.A. Morrison, Proc. Roy. Soc. (London) **A242**, 478 (1957).
[d] References 18 and 20.
[e] Reference 11.
[f] See footnote b, Vol. I, p. 66.
[g] T.H.K. Barron, W.T. Berg, and J.A. Morrison, Proc. Roy. Soc. (London) **A242**, 478 (1957), and W.T. Berg and J.A. Morrison, Proc. Roy. Soc. (London) **A242**, 467 (1957).
[h] Reference 12.
[i] Reference 18.
[j] Z. Barnea and B. Post, Acta. Cryst. **21**, 181 (1966); A.R. Taylor, Jr., T.E. Gardner, and D.G. Smith, U.S. Bureau of Mines Report of Investigations No. 6157, 1963 (unpublished).
[k] Reference 21.
[l] Reference 13.
[m] F. Hajj, J. Chem. Phys. **44**, 4618 (1966). In units of 10^{-58} erg cm^6.
[n] In units of 10^{-74} erg cm^8. J.E. Mayer, J. Chem. Phys. **1**, 270 (1933).
[o] Determined from polarizabilities (see Ref. 1) calculated by J.R. Tressman, A.H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953); J. Pirenne and E. Kartheuser, Physica **30**, 2005 (1964).

TABLE II. Calculated pressure at selected temperatures and compressions, $\Delta r/r_0$ or $\Delta V/V_0$, for NaCl.

$\Delta V/V_0$	0°	25° C	100° C	200° C	300° C	500° C	800° C	$\Delta r/r_0$
0.0		0.00	2.13	5.00	7.89	13.72	22.48	0.0
-0.0060	0.74	1.44	3.57	6.44	9.34	15.16	23.93	-0.002
-0.0120	2.24	2.94	5.06	7.93	10.83	16.65	25.43	-0.004
-0.0179	3.77	4.47	6.60	9.47	12.37	18.19	26.97	-0.006
-0.0238	5.36	6.06	8.18	11.06	13.95	19.78	28.56	-0.008
-0.0297	7.00	7.70	9.82	12.69	15.59	21.42	30.20	-0.010
-0.0356	8.68	9.38	11.51	14.38	17.28	23.11	31.89	-0.012
-0.0414	10.42	11.12	13.24	16.12	19.01	24.85	33.63	-0.014
-0.0472	12.22	12.91	15.04	17.91	20.81	26.64	35.43	-0.016
-0.0530	14.07	14.76	16.88	19.76	22.65	28.49	37.28	-0.018
-0.0588	15.97	16.67	18.79	21.66	24.56	30.40	39.19	-0.020
-0.0646	17.93	18.63	20.75	23.62	26.52	32.36	41.16	-0.022
-0.0703	19.96	20.65	22.77	25.65	28.54	34.38	43.19	-0.024
-0.0760	22.04	22.74	24.86	27.73	30.63	36.47	45.27	-0.026
-0.0817	24.19	24.88	27.00	29.87	32.77	38.61	47.42	-0.028
-0.0873	26.40	27.10	29.21	32.08	34.98	40.83	49.64	-0.030
-0.0930	28.68	29.37	31.49	34.36	37.26	43.11	51.92	-0.032
-0.0986	31.03	31.72	33.84	36.71	39.61	45.45	54.27	-0.034
-0.1042	33.44	34.13	36.25	39.12	42.02	47.87	56.69	-0.036
-0.1097	35.93	36.62	38.74	41.61	44.51	50.35	59.18	-0.038
-0.1153	38.49	39.18	41.30	44.16	47.07	52.92	61.74	-0.040
-0.1208	41.13	41.82	43.93	46.80	49.70	55.55	64.38	-0.042
-0.1263	43.84	44.53	46.64	49.51	52.41	58.26	67.10	-0.044
-0.1317	46.63	47.32	49.43	52.30	55.20	61.06	69.89	-0.046
-0.1372	49.51	50.20	52.31	55.18	58.08	63.93	72.77	-0.048
-0.1426	52.47	53.16	55.26	58.13	61.03	66.89	75.73	-0.050
-0.1480	55.51	56.20	58.31	61.17	64.08	69.93	78.77	-0.052
-0.1534	58.64	59.33	61.44	64.30	67.21	73.06	81.91	-0.054
-0.1588	61.87	62.55	64.66	67.53	70.43	76.29	85.13	-0.056
-0.1641	65.18	65.87	67.97	70.84	73.74	79.60	88.45	-0.058
-0.1694	68.59	69.28	71.38	74.25	77.15	83.01	91.86	-0.060
-0.1747	72.10	72.79	74.89	77.75	80.66	86.52	95.37	-0.062
-0.1800	75.71	76.40	78.50	81.36	84.26	90.13	98.98	-0.064
-0.1852	79.42	80.11	82.21	85.07	87.97	93.84	102.70	-0.066
-0.1904	83.24	83.93	86.02	88.89	91.79	97.65	106.52	-0.068
-0.1956	87.17	87.85	89.95	92.81	95.71	101.58	110.44	-0.070
-0.2008	91.21	91.89	93.98	96.84	99.75	105.61	114.48	-0.072
-0.2060	95.36	96.04	98.13	100.99	103.90	109.76	118.64	-0.074
-0.2111	99.63	100.31	102.40	105.26	108.16	114.03	122.91	-0.076
-0.2162	104.01	104.69	106.79	109.64	112.55	118.42	127.30	-0.078
-0.2213	108.53	109.21	111.30	114.15	117.06	122.93	131.81	-0.080
-0.2264	113.17	113.84	115.93	118.79	121.69	127.57	136.45	-0.082
-0.2314	117.94	118.61	120.70	123.56	126.46	132.33	141.22	-0.084
-0.2364	122.84	123.52	125.60	128.46	131.36	137.23	146.12	-0.086
-0.2414	127.88	128.55	130.64	133.49	136.40	142.27	151.16	-0.088
-0.2464	133.06	133.73	135.82	138.67	141.57	147.45	156.34	-0.090
-0.2514	138.38	139.06	141.14	143.99	146.89	152.77	161.67	-0.092
-0.2563	143.86	144.53	146.61	149.46	152.36	158.24	167.14	-0.094
-0.2612	149.48	150.15	152.23	155.08	157.98	163.86	172.76	-0.096
-0.2661	155.26	155.93	158.01	160.86	163.76	169.64	178.54	-0.098
-0.2710	161.20	161.87	163.94	166.79	169.70	175.58	184.48	-0.100
-0.2998	200.44	201.11	203.17	206.02	208.92	214.80	223.72	-0.112
-0.3045	207.63	208.29	210.35	213.20	216.10	221.98	230.91	-0.114
-0.3092	215.01	215.67	217.73	220.57	223.47	229.36	238.29	-0.116
-0.3139	222.59	223.26	225.31	228.15	231.05	236.94	245.87	-0.118
-0.3185	230.38	231.05	233.10	235.94	238.84	244.73	253.66	-0.120
-0.3232	238.39	239.05	241.10	243.94	246.84	252.73	261.66	-0.122
-0.3278	246.61	247.27	249.32	252.16	255.06	260.95	269.88	-0.124
-0.3324	255.06	255.72	257.77	260.60	263.50	269.39	· · ·	-0.126
-0.3369	263.74	264.39	266.44	269.28	272.17	278.06	· · ·	-0.128
-0.3415	272.65	273.31	275.35	278.19	281.08	286.97	· · ·	-0.130
-0.3460	281.81	282.46	284.51	287.34	290.23	296.12	· · ·	-0.132
-0.3505	291.21	291.87	293.91	296.74	299.63	· · ·	· · ·	-0.134
-0.3550	300.87	301.53	303.57	306.40	309.29	· · ·	· · ·	-0.136
-0.3595	310.80	311.45	313.49	316.31	· · ·	· · ·	· · ·	-0.138
-0.2758	167.30	167.97	170.05	172.90	175.80	181.68	190.59	-0.102
-0.2807	173.58	174.25	176.32	179.16	182.07	187.95	196.86	-0.104
-0.2855	180.02	180.69	182.76	185.61	188.51	194.39	203.30	-0.106
-0.2903	186.65	187.31	189.38	192.23	195.13	201.01	209.93	-0.108
-0.2950	193.45	194.12	196.18	199.03	201.93	207.81	216.73	-0.110

where V_0 is the volume at atmospheric pressure and 25 °C and γ_0 is the Grüneisen parameter under these conditions. Integrating $d\ln\theta/d\ln V = -\gamma$ and using Eq. (1) to define γ yields

$$\theta = \theta_0 e^{(\gamma_0-\gamma)/A}, \tag{2}$$

where θ_0 is the Debye temperature at atmospheric pressure and 25 °C.

Equation (5) in DDI must be rewritten in a more general manner to include the CsCl-type lattice, as well as the NaCl type. Thus, we have

$$\Phi/N_0 = -\alpha q^2/r - C/r^6 - D/r^8 + Qbe^{-r/\rho} + Q'b_-e^{-r\delta/\rho_-} + Q'b_+e^{-r\delta/\rho_+} . \tag{3}$$

All the quantities in this equation are defined in DDI except for δ which is the ratio of the next-nearest-neighbor distance to the nearest-neighbor distance, Q is the number of nearest and Q' is the number of next-nearest neighbors. As explained in DDI, with any choice of A and the other parameters considered known, one can calculate ρ and b using the experimental values of the lattice parameter and adiabatic bulk modulus at atmospheric pressure and 25 °C. The values for the bulk modulus $B_s(0)$, were taken as the best average of the measurements for NaCl,[11] KCl,[12] and CsCl[13] since 1960. The constant A was chosen by making the calculated thermal expansion and adiabatic bulk modulus vs temperature at atmospheric pressure give optimum agreement with experimental measurements of these quantities.[7,14–18] For each material, the value of A which allows the theoretical thermal expansion to match experimental expansion data is considerably smaller than the value of A that brings experimental and theoretical bulk moduli into agreement. A was chosen to give a best simultaneous fit to these two experimental results. The parameters used in the calculation are given in Table I along with an estimated uncertainty

TABLE III. Calculated pressure at selected temperatures and compressions for CsCl.

$\Delta V/V_0$	0° C	25° C	100° C	200° C	300° C	500° C	800° C	$\Delta r/r_0$
0.0		0.00	1.75	4.09	6.44	11.15	18.21	0.0
-0.0120	1.50	2.08	3.83	6.17	8.51	13.21	20.26	-0.004
-0.0238	3.74	4.32	6.06	8.39	10.73	15.41	22.45	-0.008
-0.0356	6.14	6.72	8.46	10.78	13.11	17.79	24.80	-0.012
-0.0472	8.71	9.29	11.03	13.34	15.67	20.33	27.33	-0.016
-0.0588	11.47	12.04	13.77	16.08	18.40	23.05	30.04	-0.020
-0.0703	14.41	14.98	16.71	19.01	21.33	25.97	32.94	-0.024
-0.0817	17.56	18.13	19.85	22.15	24.46	29.09	36.04	-0.028
-0.0930	20.92	21.49	23.20	25.50	27.80	32.42	39.36	-0.032
-0.1042	24.52	25.08	26.79	29.08	31.38	35.98	42.91	-0.036
-0.1153	28.35	28.91	30.62	32.90	35.19	39.79	46.69	-0.040
-0.1263	32.44	33.00	34.70	36.98	39.26	43.85	50.74	-0.044
-0.1372	36.80	37.36	39.05	41.32	43.60	48.18	55.05	-0.048
-0.1480	41.44	42.00	43.69	45.95	48.23	52.79	59.65	-0.052
-0.1588	46.39	46.95	48.63	50.89	53.16	57.71	64.55	-0.056
-0.1694	51.66	52.21	53.89	56.14	58.40	62.94	69.77	-0.060
-0.1800	57.26	57.81	59.49	61.73	63.99	68.52	75.33	-0.064
-0.1904	63.22	63.77	65.44	67.68	69.93	74.45	81.24	-0.068
-0.2008	69.56	70.11	71.77	74.01	76.25	80.76	87.53	-0.072
-0.2111	76.31	76.85	78.51	80.74	82.97	87.47	94.23	-0.076
-0.2213	83.47	84.01	85.67	87.89	90.12	94.60	101.34	-0.080
-0.2314	91.08	91.62	93.27	95.48	97.71	102.18	108.91	-0.084
-0.2414	99.17	99.71	101.35	103.55	105.77	110.23	116.94	-0.088
-0.2514	107.75	108.29	109.92	112.12	114.34	118.79	125.48	-0.092
-0.2612	116.86	117.40	119.03	121.22	123.43	127.87	134.54	-0.096
-0.2710	126.53	127.07	128.69	130.88	133.08	137.51	144.16	-0.100
-0.2807	136.80	137.33	138.95	141.13	143.32	147.73	154.38	-0.104
-0.2903	147.68	148.21	149.83	152.00	154.19	158.59	165.21	-0.108
-0.2998	159.23	159.76	161.36	163.53	165.71	170.10	176.71	-0.112
-0.3092	171.47	172.00	173.60	175.76	177.94	182.31	188.90	-0.116
-0.3185	184.45	184.98	186.57	188.72	190.89	195.26	201.83	-0.120
-0.3278	198.21	198.73	200.32	202.47	204.63	208.98	215.54	-0.124
-0.3369	212.79	213.31	214.89	217.03	219.19	223.53	230.07	-0.128
-0.3460	228.24	228.76	230.34	232.47	234.62	238.95	245.47	-0.132
-0.3550	244.61	245.13	246.70	248.83	250.97	255.29	261.79	-0.136
-0.3639	261.95	262.47	264.03	266.15	268.29	272.59	279.08	-0.140
-0.3728	280.32	280.83	282.39	284.50	286.63	290.93	297.39	-0.144
-0.3815	299.77	300.28	301.84	303.94	306.06	310.34	316.79	-0.148
-0.3902	320.37	320.88	322.42	324.52	326.64	330.91	337.34	-0.152
-0.3988	342.18	342.68	344.22	346.31	348.42	352.68	359.09	-0.156
-0.4073	365.26	365.77	367.30	369.38	371.49	375.73	382.13	-0.160
-0.4157	389.70	390.20	391.73	393.80	395.90	400.13	406.51	-0.164
-0.4241	415.56	416.06	417.58	419.65	421.74	425.96	432.32	-0.168

for each. The uncertainties in these parameters leads to an uncertainty in the calculated equation of state which was estimated by repeating the calculation while varying the parameters over their range of uncertainties. The limits on *A* are those that match the theoretical with the experimental bulk modulus and thermal expansion, respectively. The values of γ_0 shown in the table differ slightly from the values reported in the literature[19–21] but were chosen because they yielded the correct coefficient of linear thermal expansion[16–18,22,23] at $P = 0$ and $T = 25\,^{\circ}\mathrm{C}$.

TABLE IV. Comparison of calculated and measured[a] pressure along the Hugoniot for NaCl.

V/V_0	T(°K)	P_H(kbar)	P_{cal}(kbar)
0.9732	336	25	24.7
0.9546	386	50	49.0
0.9402	450	75	73.2
0.9284	527	100	97.6
0.9095	721	150	147.2
0.8945	960	200	198.3
0.8821	1238	250	250.4

[a] Smoothed results of Fritz *et al.* (Ref. 29).

RESULTS

The calculated pressure in kbars as a function of compression and temperature is given in Tables II and III for NaCl and CsCl, respectively. The selected values are spaced such as to allow linear interpolation to an accuracy better than 0.01 kbar below 100 kbar, 0.03 kbar below 150 kbar, and 0.07 kbar at higher pressures. Figure 1 compares the various contributions to the pressure along the room-temperature isotherm, while Figs. 2(a) and 2(b) show the calculated and experimental linear thermal expansion and adiabatic bulk modulus vs temperature at atmospheric pressure. It was from these curves that the value of *A* was selected. Differences between the calculated pressure and various experimental measurements[24–29] are given along the room-temperature isotherm in Fig. 3. Table IV compares the calculated pressure along the Hugoniot for NaCl to that determined by shock measurements.[29] It is noted that for all these materials the agreement is well within the experimental uncertainty except for the CsCl data of Perez-Albuerne and Drickamer. Table V compares the experimentally measured[2,3,30] equilibrium values of the pres-

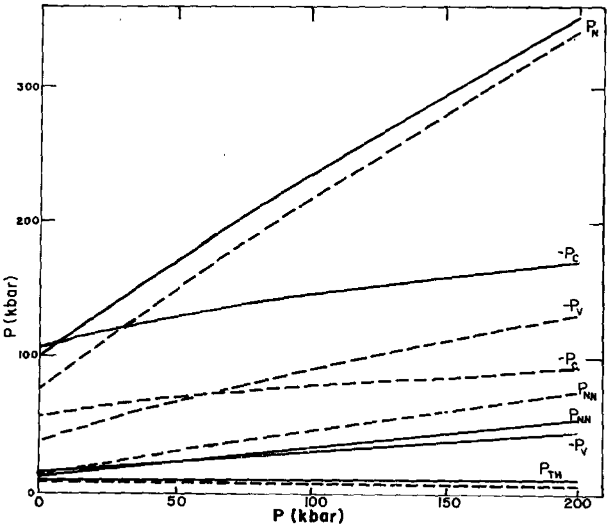

FIG. 1. Contribution to the pressure from the nearest-neighbor repulsion P_N, the second-nearest-neighbor repulsion P_{NN}, the thermal vibration P_{TH}, the coulomb attraction P_C, and the Van der Waals attraction P_V, as functions of pressure for NaCl (solid lines) and CsCl (dashed lines).

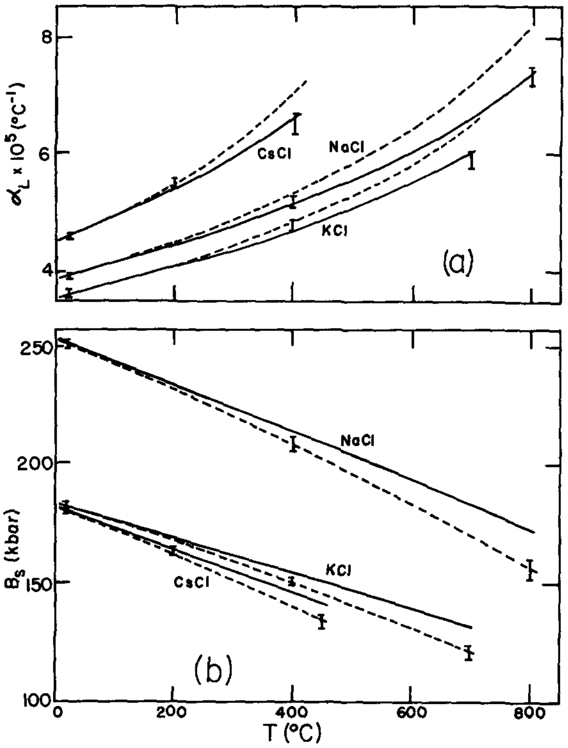

FIG. 2. (a) Coefficient of linear thermal expansion vs temperature and (b) the adiabatic bulk modulus vs temperature, both at atmospheric pressure. The vertical bars indicate the uncertainty of measured values, the solid lines are calculated using the optimum logrithmic volume coefficient (*A*) of the Grüneissen parameter to fit the expansion data, while the dashed lines are calculated using the value of *A* chosen to best fit the bulk modulus data. The value of *A* chosen for the equation-of-state calculations was intermediate between these extremes.

sure at the Bi (I-II), Ba (I-II), and Bi (III-V) phase transitions to the values calculated from the measurements of the NaCl compression at these points by Jeffery *et al.*[4] The value taken from the measurements of the Ba transition by Haygarth *et al.*[2] is for his less pure material to correspond to the material used by Jeffery *et al.* Inoue[31] has repeated the work of Jeffery *et al.* with substantial agreement with their their work.

TABLE V. Measured and calculated pressure at selected phase transitions.

Experimental	25.49 ± 0.06[a]	54.7 ± 0.5[b]	77.5 ± 1.0[c]
Calculated[d]	25.32 ± 0.77	54.7 ± 1.3	76.0 ± 1.8
Calculated[e]	25.21 ± 0.33	54.1 ± 0.6	75.1 ± 0.6

[a] See Ref. 30.

[b] See Ref. 2. for the less pure material.

[c] See Ref. 3.

[d] Calculated at the measured compression of NaCl (see Ref. 4) at these phase boundaries. The uncertainties include both these from the measured compression and from the theory but no estimate of uncertainty due to the uncertainty in choosing the equilibrium value at the center of the hysteresis.

[e] The same as d but for the date of Inoue (Ref. 31). His estimated errors are likely too small.

The cohesive energy at 25 °C and atmospheric pressure for NaCl, KCl, and CsCl were calculated to be − 183.2 ± 0.3, − 166.6 ± 0.2, and − 154.8 ± 0.3 kcal/mole, respectively. These are in excellent agreement with the experimental values of − 182.9 ± 1.4, − 167.5 ± 1.6, and − 156 ± 4 kcal/mole,[34-34] respectively. Thus the electron affinity is in excellent agreement with experiment, but until the experiments become more precise this does not constitute a decisive test of the theory.

DISCUSSION AND CONCLUSIONS

This type of calculation gives an excellent equation of state for alkali halides as far as *P-V-T* measurements are concerned; however, it could not be trusted to yield accurate values of higher-order derivatives of thermodynamic variables as attested by the fact that one cannot choose a single value of the parameter *A* that will simultaneously yield good values for the coefficient of linear thermal expansion and the adiabatic bulk modulus over a range of temperatures. The calculated pressure however is quite accurate even at elevated temperatures. This, most likely, is due to the fact that for temperatures even as high as 2000 °C the thermal contribution to

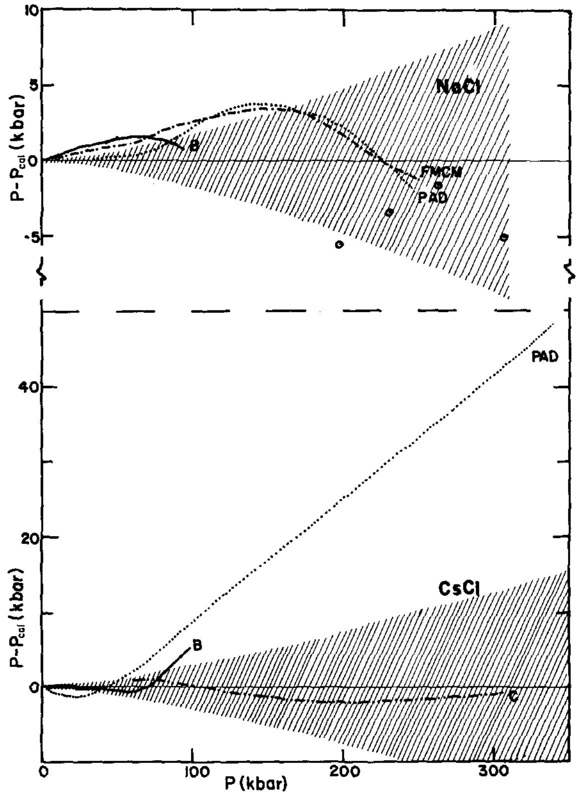

FIG. 3. Differences between the calculated pressure from the equation of state and measurements of Bridgman: B; Perez-Albuerne and Drickamer: PAD; Fritz, Marsh, Carter, and McQueen: FMCM; Weaver, Takahashi, and Bassett: ⊙, and Christian: C. See text for references. The diverging dashed lines indicate the uncertainty in the calculation resulting from uncertainties in the measured input parameters.

TABLE VI. Comparison of measured and calculated pressure.

Pressure (meas)[a] (kbar)	NaCl pressure (calc) (kbar)	CsCl pressure (calc) (kbar)	LiF pressure (calc) (kbar)
15	15.34	14.85	15.35
30	30.21	29.68	30.14
45	45.19	44.56	43.93

[a] See Ref. 36.

the pressure is still rather small compared to other contributions. Due to uncertainty in the input parameters, but not including any approximation inherent in the theory, the uncertainty of the calculated result is 1.1% below 50 kbar, 1.7% below 100 kbar, and 2.4% below 200 kbar. About $\frac{2}{3}$ of this estimated error in the pressure calculation comes from the uncertainty in the volume dependence of the Grüneisen parameter. The uncertainty in the calculation is presently of the same order of magnitude as the attainable accuracy for measured pressures and so one cannot be guided from experiment as to how to improve on the present theory. Thompson[35] has objected to this theoretical approach by making the argument that the energy eigenvalue spectrum is not consistent with the form of the interatomic potential. This objection is correct but again, as far as P-V-T measurements are concerned, the kinetic-energy contribution to the pressure is small enough that only a rough approximation to this term yields an accurate equation of state. The vital concern for this type of a calculation is to have a good approximation to the interatomic potential, which is the failing with Thomson's "consistent" approach.

Both the NaCl and CsCl equations of state are in excellent agreement with dynamic measurements using shock techniques. For NaCl the agreement is a little better along the Hugoniot than for the isotherm determined by Fritz *et al.*[29] from their measured Hugoniot. It is apparent that the volume dependence of γ used in this theory is similar to the Dugdale-McDonald formula used by Fritz *et al.* These equations are in excellent agreement with the compression measurements of Bridgman to 100 kbar for NaCl and CsCl. If Bridgman's results on NaCl, KCl, and CsCl are consistent with each other, then this agreement gives confirmation to the theory.

Some recent measurements by Vaidya and Kennedy[36] of compression vs pressure has come to our attention. Taking their measured value of V/V_0, I have calculated P at 25 °C for several materials and compared them to their measured pressures in Table VI. The agreement for NaCl and CsCl is extremely good and well within the uncertainties, and even that for LiF is as good as could be expected to these pressures.

Another comparison is possible using the argument that the Murnaghan two-parameter equation should be accurate for relatively small compression, and thus should yield accurate pressures for a noncompressible material such as MgO. Simultaneous measurements of MgO and NaCl compression have been made by McWhan[5] and Weaver *et al.*[25] The pressure calculated from the MgO compression agrees very well with the pressure determined by this equation of state from the compression of NaCl. The NaCl compression, measured by Bassett *et al.*[37] yields a value of 302 ± 9 kbar at the NaCl transition to the CsCl phase, compared to 307 ± 10 kbar determined by the MgO compression via the Murnaghan equation at that point.

The calculation for both NaCl and CsCl allows a direct experimental consistency check by simultaneously making x-ray measurements at high pressures on intimately mixed powders of NaCl and CsCl. Such a comparison has been made between NaCl and LiF. Both the experimental work[38] and the calculated equation of state for LiF are of such dubious nature that no definite conclusions can be drawn.

The accuracy of this theory is comparable to our present experimental capability so that it seems sufficient until more precise volume measurements can be made at high pressures. One advantage of using this approach to pressure calibration is that it is simple to convert experimental data to a new pressure scale when a more accurate scale is defined.

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