

TABLE I. Various equations of state.

Equation	Acronym	Form
First-order Murnaghan	ME <sub>1</sub>	$z = \eta^{-1} (x^2 - 1)$
Second-order Murnaghan	ME <sub>2</sub>	$z = 2 (\eta^2 - 2\psi)^{1/2} - 1 / \times [(\eta^2 - 2\psi)^{1/2} (x(\eta^2 - 2\psi)^{1/2} + 1) - \eta (x(\eta^2 - 2\psi)^{1/2} - 1)]$
Keane	KE	$z = [\eta^3 / (\eta^2 + \psi)^2] \times (x(\eta^2 + \psi) / \eta - 1) - [\psi / (\eta^2 + \psi)] \ln x$
First-order Birch	BE <sub>1</sub>	$z = \frac{3}{2} (x^{7/3} - x^{5/3}) \times [1 + \frac{3}{4} (\eta - 4) (x^{2/3} - 1)]$
Second-order Birch	BE <sub>2</sub>	$z = \frac{3}{2} [x^{7/3} - x^{5/3}] \times [1 + \frac{3}{4} (\eta - 4) (x^{2/3} - 1) + \frac{1}{24} [143 + 9\eta (\eta - 7) + 9\psi] \times (x^{2/3} - 1)^2]$
Grover, Getting, Kennedy	GGKE	$B_T = B_0^T \exp[\eta (1 - x^{-1})]$

two-parameter equations, the standard deviation of the  $V/V_0$ -vs- $P$  fit is less for the three-parameter equations. The weighted averages of the parameters  $B_0$ ,  $B'_0$ , and  $B''_0$  as determined by the two- and three-parameter equations of state are listed in Table IV. Also included in Table IV are the results of previous experiments for the purpose of comparison.

#### IV. DISCUSSION

##### A. Comparison with previous results

As can be seen from Table IV, present measurements of  $B_0$  and  $B'_0$  are not in agreement with those obtained earlier from static-compression techniques. The piston displacement method used by Vaidya and Kennedy is subject to errors caused by the finite yield strength of the NaCl, which is assumed to be absent and zero.

TABLE II. Bulk modulus and its pressure derivatives at 29.5°C.

Equation used <sup>a</sup>	$B_0$ (kbar)	$B'_0$	$B''_0$ (kbar <sup>-1</sup> )	Run No.
ME <sub>1</sub>	238.14 ± 0.10	5.57 ± 0.04	0.00 <sup>b</sup>	1
	238.20 ± 0.12	5.60 ± 0.05	0.00	2
ME <sub>2</sub>	237.72 ± 0.24	5.95 ± 0.20	-0.11 ± 0.10	1
	237.89 ± 0.20	5.96 ± 0.20	-0.13 ± 0.15	2
GGKE	238.07 ± 0.08	5.64 ± 0.04	-0.024 <sup>b</sup>	1
	238.18 ± 0.11	5.66 ± 0.05	-0.024 <sup>b</sup>	2
BE <sub>1</sub>	238.04 ± 0.08	5.68 ± 0.04	-0.035 <sup>b</sup>	1
	238.15 ± 0.11	5.69 ± 0.05	-0.035 <sup>b</sup>	2
BE <sub>2</sub>	237.72 ± 0.24	5.97 ± 0.22	-0.13 ± 0.10	1
	237.90 ± 0.22	5.97 ± 0.22	-0.14 ± 0.15	2
KE	237.71 ± 0.24	5.98 ± 0.20	-0.14 ± 0.10	1
	237.89 ± 0.22	5.98 ± 0.24	-0.15 ± 0.15	2

<sup>a</sup>Acronyms defined in Table I.

<sup>b</sup>Obtained from  $B_0$  and  $B'_0$  using the appropriate expression given in Ref. 27.

TABLE III. Bulk modulus and its pressure derivatives at 40.4°C.

Equation used <sup>a</sup>	$B_0$ (kbar)	$B'_0$	$B''_0$ (kbar <sup>-1</sup> )	Run No.
ME <sub>1</sub>	236.68 ± 0.08	5.53 ± 0.03	0.00 <sup>b</sup>	1
	236.66 ± 0.09	5.51 ± 0.03	0.00 <sup>b</sup>	2
	236.43 ± 0.32	5.55 ± 0.112	0.00 <sup>b</sup>	3
ME <sub>2</sub>	236.56 ± 0.22	5.65 ± 0.18	-0.04 ± 0.06	1
	236.28 ± 0.15	5.85 ± 0.13	-0.10 ± 0.15	2
	236.18 ± 0.41	5.78 ± 0.35	-0.07 ± 0.20	3
GGKE	236.61 ± 0.08	5.61 ± 0.03	-0.024 <sup>b</sup>	1
	236.60 ± 0.08	5.58 ± 0.03	-0.024 <sup>b</sup>	2
	236.37 ± 0.33	5.62 ± 0.12	-0.024 <sup>b</sup>	3
BE <sub>1</sub>	236.59 ± 0.08	5.63 ± 0.03	-0.035 <sup>b</sup>	1
	236.56 ± 0.08	5.61 ± 0.03	-0.035 <sup>b</sup>	2
	236.33 ± 0.34	5.65 ± 0.12	-0.035 <sup>b</sup>	3
BE <sub>2</sub>	236.58 ± 0.22	5.64 ± 0.20	-0.04 ± 0.07	1
	236.28 ± 0.16	5.87 ± 0.14	-0.12 ± 0.15	2
	236.19 ± 0.43	5.78 ± 0.38	-0.08 ± 0.24	3
KE	236.58 ± 0.22	5.64 ± 0.20	-0.04 ± 0.07	1
	236.27 ± 0.16	5.88 ± 0.14	-0.13 ± 0.15	2
	236.18 ± 0.44	5.79 ± 0.39	-0.08 ± 0.25	3

<sup>a</sup>Acronyms defined in Table I.

<sup>b</sup>Obtained from  $B_0$  and  $B'_0$  using the appropriate expression given in Ref. 27.

Singh and Kennedy<sup>28</sup> on the basis of x-ray studies suggest that the yield stress is quite high so that sizable deviatoric stresses are present. Ruoff<sup>29</sup> gives an estimate of the yield stress much smaller than Singh and Kennedy; nevertheless, even the presence of this yield stress would cause a sizable variation in the measured values of  $B_0$  and particularly  $B'_0$  using the piston displacement method. However, Kinsland and Bassett<sup>30</sup> in their x-ray studies do not observe a finite yield stress. It is conceivable that in the very long exposure time used by them considerable thermally activated stress relaxation occurred.

The agreement is fairly good when compared with ultrasonic measurements. The values obtained from  $B'_0$  ultrasonically are generally lower than the present values, although they would tend to agree within the experimental uncertainties. In most of the ultrasonic work, errors are not listed with the data. Ghafelehbashi and Koliwad<sup>7</sup> note that their values for derivatives of the individual directly measured elastic constants are good to within 5%. Since  $B$  involves a sum of two measured elastic constants ( $B = C_{11} - \frac{1}{3} C_{33}$ ),  $B'_0$  does likewise. Hence the potential for error is even larger. Even if an error of only 2.5% is used for the individual measured derivatives, the error in  $B'_0$  would be about ±0.4. Most of these ultrasonic measurements were carried out only to a maximum of 3 to 4 kbar. Generally the data were analyzed by ignoring the contribution of  $B''_0$  (except for Spetzler *et al.*) and therefore they would generally tend to yield lower values of  $B'_0$ ; this neglect, for  $B''_0 = -0.1$  kbar<sup>-1</sup>, would lead to an ultrasonic value of  $B'_0$  too low by about 0.2. One can compute a value of -0.09 kbar<sup>-1</sup> for  $B''_0$  from the data of Spetzler *et al.*,<sup>9</sup> and our measurements give an average value of -0.10 kbar<sup>-1</sup>. Considering the large uncertainties involved, the agreement is rather astonishing.



TABLE IV. Comparison of isothermal bulk modulus and its pressure derivative with previous values.

Source	Technique	$B_0$ (kbar)	$B'_0$	$B''_0$ (kbar <sup>-1</sup> )
Present work <sup>a</sup>	Length	238.1	5.64	
Present work <sup>b</sup>	Length	237.7	5.97	-0.12
Present work <sup>c</sup>	Length	237.7	5.71	-0.10
Present work <sup>d</sup>	Length	237.8	5.85	-0.12
Haussühl	Ultrasonic	237.3		
Ghafelehbash and Koliwad	Ultrasonic	237.0	5.37	
Barsch and Chang	Ultrasonic	234.2	5.39	
Spetzler <i>et al.</i>	Ultrasonic	238.0	5.35	-0.09
Bartels and Schuele	Ultrasonic	234.0	5.35	
Bridgman	Piston-volume	240.8	4.61	
Vaidya and Kennedy	Piston-volume	231.7	4.92	
Fritz <i>et al.</i>	Shock	237.3 <sup>e</sup>	5.50	

<sup>a</sup>A weighted average of the two-parameter equations at  $T=29.5^\circ\text{C}$ .

<sup>b</sup>A weighted average of the three-parameter equations at  $T=29.5^\circ\text{C}$ .

<sup>c</sup>A weighted average for the parameters  $B'_0$  from all equations and  $B''_0$  from all the three-parameter equations at  $T=29.5$  and  $40.4^\circ\text{C}$ .

<sup>d</sup>A weighted averaged for the parameters  $B'_0$  and  $B''_0$  from Keane's equation at  $T=29.5$  and  $40.4^\circ\text{C}$ .

<sup>e</sup>This value was not measured by them; instead Haussühl's value was used.

## B. Discussion of $B''_0$

The most interesting result of this experiment is the determination of  $B''_0$ . The weighted average value for  $B''_0$  as indicated in Table IV is  $-0.10 \pm 0.05 \text{ kbar}^{-1}$ . Admittedly  $B''_0$  has a large error associated with it. The main source of error in determining  $B''_0$  is the pressure itself. As pointed out before,<sup>27</sup> the magnitude of  $B''_0$  depends on the functional form of the variation of  $P$  with the change in resistance per unit resistance ( $\Delta R/R_0$ ) of the manganin gauge. As shown in Table V if one makes the assumption that the nonlinear pressure variation with the change in resistance of the manganin gauge is cubic, the weighted average value for  $B''_0$  is then  $-0.03 \text{ kbar}^{-1}$ . Table V is included in the text to emphasize the sensitivity of  $B''_0$  to the possible uncertainty in pressure in this low-pressure region. What evidence is

TABLE V. Isothermal bulk modulus and its pressure derivative based on the assumption that the nonlinear pressure variation with the change in resistance of the manganin gauge is cubic.

$B_0$ (kbar)	$B'_0$	$B''_0$ (kbar <sup>-1</sup> )
238.20 <sup>a</sup>	5.60 <sup>a</sup>	
238.00 <sup>b</sup>	5.75 <sup>b</sup>	-0.06 <sup>b</sup>
238.00 <sup>c</sup>	5.53 <sup>c</sup>	-0.03 <sup>c</sup>

<sup>a</sup>A weighted average of the two-parameter equation at  $T=29.5^\circ\text{C}$ .

<sup>b</sup>A weighted average of the three-parameter equations at  $T=29.5^\circ\text{C}$ .

<sup>c</sup>A weighted average for the parameters  $B'_0$  from all equations and  $B''_0$  from all the three-parameter equations at  $T=29.5$  and  $40.4^\circ\text{C}$ .

presently available (free piston data to 40 kbar)<sup>31</sup> suggests that of three possible fits to the nonlinear term, quadratic, quadratic and cubic, and cubic, the quadratic fit is best. This does not rule out other important possibilities and must be considered an area where new developments and extra precision are needed. However, these results would indicate that  $B''_0$  is more likely to be  $-0.10 \text{ kbar}^{-1}$ . As expected, the dependence of  $B''_0$  on the pressure variation of the manganin gauge is not as sensitive for low-bulk-modulus materials (e.g., sodium, potassium) as it is for high-bulk-modulus materials. The data for LiF indicates<sup>27</sup> even a much more sensitive dependence on the functional form of the gauge than NaCl does:  $B''_0$  is related to the third pressure derivative of a function expressing the pressure in terms of the volume. Hence any error that is inherent in the pressure-vs-volume measurements will be propagated and compounded when  $B''_0$  is computed. In other words the pressure-volume measurement must be extremely precise. The present  $V/V_0$  measurements already have a precision of  $1 \times 10^{-7}$ . It is the pressure that we know only to a precision of  $1 \times 10^{-4}$ , as the mercury point<sup>32</sup> is known only to 1 bar. Hence unless the pressure is measured to an extremely high precision of  $1 \times 10^{-6}$ , the error in  $B''_0$  is going to remain at a relatively large magnitude.

## C. Transition pressures of some fixed points

Using the values of  $B_0$ ,  $B'_0$ ,  $B''_0$  that are listed in Table IV, the pressure transitions for the following transformations are estimated on the basis of two- and three-parameter equations of state and are tabulated in Table VI: (i) the barium I-II transformation, (ii) the bismuth III-V transformation, (iii) the transformation of bcc-phase iron to hcp phase, (iv) the transformation of NaCl itself from the NaCl to the CsCl structure.

The experimental values of  $V/V_0$  used to estimate the

TABLE VI. Transformation pressures for some transitions and its comparison with previous values.

Equation used <sup>a</sup>	Ba I-II	Bi III-V <sup>b</sup>	Fe transition (kbar)	NaCl transition
ME <sub>1</sub> <sup>b</sup>	59.9	86.2	170	468
BE <sub>1</sub> <sup>b</sup>	58.0	81.7	153	362
GGKE <sup>b</sup>	58.3	82.4	154	356
ME <sub>2</sub> <sup>c</sup>	52.1	67.5	96	120
BE <sub>2</sub> <sup>c</sup>	54.9	74.4	121	173
KE <sup>c</sup>	55.8	76.8	134	271
ME <sub>2</sub> <sup>d</sup>	52.3	68.7	100	132
BE <sub>2</sub> <sup>d</sup>	54.6	74.3	122	196
KE <sup>d</sup>	55.4	76.2	132	274
KE <sup>e</sup>	55.3	75.8	130	262
KE <sup>f</sup>	54.1	74.0	136	258
Decker	54.7	76.4	136	306
Drickamer		73-75	(110-113)	
Ref. 37	55	77		

<sup>a</sup>Acronyms defined in Table I.

<sup>b</sup>The values used for  $B_0$ ,  $B'_0$ , and  $B''_0$  are defined by footnote a in Table IV.

<sup>c</sup>Values defined by footnote b in Table IV.

<sup>d</sup>Values defined by footnote c in Table IV.

<sup>e</sup>Values defined by footnote d in Table IV.

<sup>f</sup>Indicates that the values for  $B_0$ ,  $B'_0$ , and  $B''_0$  obtained by Spetzler *et al.*, that are listed in Table IV, were used.