# Isothermal equation of state for sodium chloride by the length-change-measurement technique

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The change in length of a 1-m-long NaCl single crystal has been determined as a function of hydrostatic pressure up to 7.5 kbar and at temperatures of 29.5 and 40.4°C, to an accuracy of 500 Å using a Fabry-Perot-type He-Ne laser interferometer. The best values of the isothermal bulk modulus and its pressure derivative at atmospheric pressure and at 29.5°C are  $B_0 = 237.7 \pm 0.3$  kbar,  $B'_0 = 5.71 \pm 0.25$ , and  $B''_0 = -0.10 \pm 0.05$  kbar<sup>-1</sup>, respectively. These are the averages of the values obtained by a least-squares fit of several different equations of state to the present isothermal data. From these low-pressure measuements alone, it is not possible to conclude which one of these equations provides a better fit to the data than the others. However, when other high-pressure data are taken into account, it appears that Keane's equation best represents the measurements. When Keane's equation is fitted to the data, and the published lattice parameter of NaCl at the Bi-III-V transition and at the NaCl B1-B2 transition are used, the respective transition pressures are found to be 75.8 kbar, within 1.2 kbar of the presently accepted value and 262 kbar, respectively. Considering the precision of the experiment the values of  $B_0$ ,  $B'_0$ , and  $B''_0$  represent the best measurements so far. The determination of  $B''_0$  isothermally represents the first measurement of its kind.

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## I. INTRODUCTION

There is considerable interest in high-pressure laboratories to develop static high pressures in excess of 500 kbar. What was once believed to be in excess of 500 kbar.<sup>1</sup> has now been scaled down to approximately 200 kbar.<sup>2</sup> In other words, there is considerable need and interest for an accurate pressure gauge. Because of its relative ease in handling, and also because it has a low bulk modulus and in addition as there is already some x-ray data,<sup>3</sup> ultrasonic data,<sup>4-9</sup> static-compression data,<sup>10,11</sup> and shock-wave data,<sup>12</sup> NaCl has emerged as a strong candidate for use as a pressure gauge.

Jamieson<sup>13</sup> first used NaCl as an internal pressure standard in his x-ray apparatus. Since then Decker<sup>14,15</sup> has calculated a Mie-Grüneisen equation of state for NaCl based on the Born-Mayer potential. Piermarini et al.<sup>16</sup> have used Decker's equation of state to calibrate the pressure dependence of the  $R_1$  ruby fluorescence line. However, one of the difficulties with Decker's equation of state is that it yields a theoretical value of 4.93 for  $B'_0$ . Recent ultrasonic measurements<sup>4-8</sup> yield a value of 5.35 for  $B'_0$ , whereas the static-com-pression data of Bridgman<sup>10</sup> and Vaidya and Kennedy<sup>11</sup> give 4.61 and 4.92, respectively. From the shock-wave data<sup>12</sup> of Fritz *et al.* one can calculate  $B'_0$  to be 5.50. Such a wide discrepancy in experimental values for  $B'_0$  and its apparent disagreement with the value obtained from Decker's equation of state, prompted us to determine the parameters  $B_0$  and  $B'_0$  more precisely, especially because Decker's equation of state is now extensively used as a pressure gauge. Besides many researchers<sup>12,17</sup> have expressed the need for an accurate  $B'_0$ , because such a wide range of  $B'_0$  does not give guidance to theorists to improve their theories.

To obtain  $B_0$  and  $B'_0$  from ultrasonic measurements one has to transform the adiabatic bulk modulus and its pressure derivative using Overton's relations.<sup>18</sup> Additionally, one can always question the nature of the bond involving the transducer and the sample in ultrasonic experiments due to differential compressibilities. Hence to eliminate these errors we decided to measure  $B_0$  and  $B'_0$  directly by using the length-measurement system devised by Lincoln and Ruoff, <sup>19</sup> as it is capable of measuring  $V/V_0$  to a precision of  $1 \times 10^{-7}$ . Admittedly by doing ultrasonic measurements one is indeed a pressure derivative ahead when compared to length measurements.<sup>20</sup> However, in the present instance that advantage is nullified due to the fact that the length measurements are carried out to such high precision. In the final analysis, the precision to which  $B_0$  and  $B'_0$  are measured turn out to be even better or at least comparable to what one would obtain from ultrasonic measurements.

### **II. EXPERIMENTAL PROCEDURE**

A 1-m-long single crystal of NaCl was obtained from the crystal growing facility of the Cornell Materials Science Center. The specimen was chemically machined and shaped on a chemical lathe<sup>21</sup> so that it could be supported on the axis of the pressure vessel by ball bushings and is shown schematically in Fig. 1. The ends of the specimen had to be rounded off so that each end fits snugly into the magnetic cores which were machined from Kovar rods. The web thickness for these cores is 0.005 cm. The core web is kept in contact with the specimen end by spring loading using very soft Be-Cu springs.

Linear variable differential transformers (LVDT's) at atmospheric pressure surround the nonmagnetic pressure vessel and are used to locate the axial position of the magnetic cores. The ambient pressure LVDT's can be translated until they are nulled on the core centroids for both specimen ends every time a length-change measurement is made.

As shown in Fig. 1, each interferometric mirror is positioned in the center of a coupling plate such that the reflecting surface and the core centroid form a plane that is perpendicular to the specimen axis. The LVDT's

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FIG. 1. Schematic of length-measurements system: (a) laser path vacuum bellows; (2) laser beam;
(3) interferometer mirrors;
(4) coupling plates; (5) LVDT's
(6) pressure vessel; (7) specimen;
(8) magnetic cores; (9) ball bushings.

are mounted near the bottom end of these coupling plates. The coupling plates are mounted on carriages which move on a track parallel to the specimen axis. The carriage is translated by an electrically driven coarse micrometer, a fine micrometer, and finally by a piezoelectric ceramic device which has a resolution of 100 Å and a range of 10<sup>4</sup> Å. Thus displacement coupling through the pressure gradient is accomplished by using magnetic cores located at both ends of the specimen inside the pressure vessel, and by nulling these markers with LVDT's which are coupled and translated together with an optical interferometer. The path between the interferometric mirrors is kept at a vacuum pressure of a few microns. It provides a stabilized laser vacuum wavelength and is used both as a temperature-independent reference length and as a standard wave length for the relative length-change-measurement interferometer. A detailed description of the interferometer system is given in Fig. 7 of Ref. 19.

As shown in Fig. 1 the specimen is not of one uniform diameter. However, to measure the length change of the specimen along its cylindrical axis, it is not necessary for it to be of uniform cross section. On the other hand, to know the  $V/V_0$  measurement to a precision of  $1 \times 10^{-7}$ , one has to account and correct for the web thickness of the magnetic core material at each pressure. This can be easily done by knowing the bulk modulus of the core material. Also, one has to make corrections for the end-to-end specimen strain caused by spring loading. This can also be estimated to within required accuracies through the knowledge of the spring constant of the spring, the decreased length of the specimen combined with the increased length of the pressure vessel, and the Young's modulus of the specimen.

To maintain such high precision, it also becomes necessary to keep the thermal noise to a minimum. This is achieved by controlling the temperature environment of the specimen to within a few millidgrees. A detailed description of the temperature control and monitoring system is given in Fig. 8 of Ref. 19.

Liquid hexane is used as a pressure fluid and is transmitted through a pressure tubing (0.475 cm od and 0.063 cm id) to the pressure vessel. Connected in series with the length-measurement pressure vessel is another pressure vessel where manganin wire, the pressure sensor, is kept. The technique used to calibrate the manganin gauge is described in detail elsewhere.<sup>20</sup>

The length measurements were made at an interval of 500 bar up to a maximum of 7.5 kbar at each temperature. The experiment at each temperature was carried out at least twice to check for the reproducibility of the data. Inasmuch as the linear compressibility for NaCl is isotropic, the length-measurement data is transformed to volume measurements using the relation  $V/V_0 = (l/l_0)^3$ . For equation of state measurements, one is never concerned with  $V_0$  itself but only the ratio  $V/V_0$ . Consequently it is neither necessary to measure the specimen diameter nor to have a uniform diameter.

## **III. RESULTS**

Let V denote the volume of a specimen and P the pressure applied to it at some constant temperature T. Then an isothermal bulk modulus B is defined as  $B = -V(\partial P/\partial V)_T$  which at a given reference pressure  $P_0$  shall be  $B_0 = -V_0(\partial P/\partial V)_{P=P_0}$ . The first and second pressure derivative of the bulk modulus evaluated at  $P = P_0$  shall be denoted by  $B'_0$  and  $B''_0$ , respectively. For convenience, we shall introduce the following notations:  $p = P - P_0$ ,  $\eta = B'_0$ ,  $\psi = B_0 B''_0$ ,  $Z = p/B_0$ , and  $x = V_0/V$ . Note that  $\eta, \psi$ , z, and x are all dimensionless quantities.

The two- and three-parameter phenomenological equations of state $^{22-26}$  used to analyze the experimental pressure volume data are listed in Table I. The results of this least-square analysis are tabulated in Tables II and III for the two temperatures 29.5 and 40.4 °C, respectively. ME, is the only equation of state in that list for which  $B_0''$  identically equals zero. The expressions for BE<sub>1</sub> and GGKE do not explicitly contain the parameter  $B_0^{"}$ . The appropriate expression was used<sup>27</sup> in each case to calculate the values for  $B_0''$  and are also tabulated in Tables II and III, respectively. The experiment was carried out twice at 29.5°C and three times at 40.4 °C not only to check for the reproducibility of the data but also to determine a reliable value for the parameters  $B'_0$  and  $B''_0$ . As can be seen from Tables II and III, the reproducibility of the data at each temperature is excellent. It should be noted here that although the standard deviations associated with  $B_0$  and  $B'_0$  are larger for the three-parameter equations than for the

TA	BLE	I.	Various	equations	of	state.
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Equation	Acronym	Form
First-order Murnaghan	ME1	$z = \eta^{-1} \left( x^{\eta} - 1 \right)$
Second-order	ME <sub>2</sub>	$z = 2 (x^{(\eta^2 - 2\psi)^{1/2}} - 1)/$
Murnaghan	$(\eta^2 \ge 2\psi)$	$ \times [ (\eta^2 - 2\psi)^{1/2} (\chi^{(\eta^2 - 2\psi)^{1/2} + 1})  - \eta (\chi^{(\eta^2 - 2\psi)^{1/2}} - 1) ] $
Keane	KE	$z = [\eta^3 / (\eta^2 + \psi)^2]$
	$(-\eta^2 < \psi < 0)$	$\times (x^{(\eta^2 + \psi)/\eta} - 1) - [\psi/(\eta^2 + \psi)] \ln x$
First-order	BE1	$z = \frac{3}{2} \left( x^{7/3} - x^{5/3} \right)$
Birch		$\times [1 + \frac{3}{4} (\eta - 4) (x^{2/3} - 1)]$
Second-order	BE2	$z = \frac{3}{2} [x^{7/3} - x^{5/3}]$
Birch		$\times \{1 + \frac{3}{4}(\eta - 4) (x^{2/3} - 1)\}$
		$\frac{1}{24} [143 + 9\eta (\eta - 7) + 9\psi] \times (x^{2/3} - 1)^2]$
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 <sub>0</sub> (kbar)	B <sub>0</sub> '	B <sub>0</sub> " (kbar <sup>-1</sup> )	Run No.
MEi	$238.14 \pm 0.10 \\ 238.20 \pm 0.12$	$5.57 \pm 0.04$ $5.60 \pm 0.05$	0.00 <sup>b</sup> 0.00	1 2
ME <sub>2</sub>	$237.72 \pm 0.24 \\ 237.89 \pm 0.20$	$5.95 \pm 0.20$ $5.96 \pm 0.20$	$-0.11 \pm 0.10$ $-0.13 \pm 0.15$	1 2
GGKE	$238.07 \pm 0.08 \\ 238.18 \pm 0.11$	$5.64 \pm 0.04$ $5.66 \pm 0.05$	-0.024 <sup>b</sup> -0.024 <sup>b</sup>	1 2
BE1	$238.04 \pm 0.08 \\ 238.15 \pm 0.11$	$5.68 \pm 0.04 \\ 5.69 \pm 0.05$	-0.035 <sup>b</sup> -0.035 <sup>b</sup>	1 2
BE2	$237.72 \pm 0.24 \\ 237.90 \pm 0.22$	$5.97 \pm 0.22$ $5.97 \pm 0.22$	$-0.13 \pm 0.10$ $-0.14 \pm 0.15$	1 2
KE	$237.71 \pm 0.24$ $237.89 \pm 0.22$	$5.98 \pm 0.20$ $5.98 \pm 0.24$	$-0.14 \pm 0.10$ $-0.15 \pm 0.15$	1 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 <sub>0</sub> (kbar)	B <sub>0</sub> '	<i>B</i> <sub>0</sub> " (kbar <sup>-1</sup> )	Run No.
ME <sub>1</sub>	$236.68 \pm 0.08$	$5.53 \pm 0.03$ $5.51 \pm 0.03$	0.00 <sup>b</sup>	1
	$236.43 \pm 0.32$	$5.55 \pm 0.112$	0.00 <sup>b</sup>	3
ME <sub>2</sub>	$236.56 \pm 0.22$	$5.65 \pm 0.18$	$-0.04 \pm 0.06$	1
	$236.28 \pm 0.15$ $236.18 \pm 0.41$	$5.85 \pm 0.13$ $5.78 \pm 0.35$	$-0.10 \pm 0.15$ $-0.07 \pm 0.20$	23
GGKE	$236.61 \pm 0.08$	$5.61 \pm 0.03$	-0.024 <sup>b</sup>	1
	$236.37 \pm 0.33$	$5.62 \pm 0.12$	$-0.024^{b}$	3
BE1	$236.59 \pm 0.08$	$5.63 \pm 0.03$	-0.035 <sup>b</sup>	1
	$236.56 \pm 0.08$ $236.33 \pm 0.34$	$5.61 \pm 0.03$ $5.65 \pm 0.12$	$-0.035^{b}$ $-0.035^{b}$	2
BE2	$236.58 \pm 0.22$	$5.64 \pm 0.20$	$-0.04 \pm 0.07$	1
	$236.28 \pm 0.16$ $236.19 \pm 0.43$	$5.87 \pm 0.14$ $5.78 \pm 0.38$	$-0.12 \pm 0.15$ $-0.08 \pm 0.24$	23
KE	$236.58 \pm 0.22$	$5.64 \pm 0.20$	$-0.04 \pm 0.07$	1
jo ej	$236.27 \pm 0.16 \\ 236.18 \pm 0.44$	$5.88 \pm 0.14 \\ 5.79 \pm 0.39$	$-0.13 \pm 0.15 \\ -0.08 \pm 0.25$	2 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  $(B = C_1 - \frac{4}{3}C_s)$ ,  $B'_0$  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  $\pm 0.4$ . 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 -0.10kbar<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 <sub>0</sub> (kbar)	B <sub>0</sub>	<i>B</i> <sub>0</sub> " (kbar <sup>-1</sup> )
Present work <sup>a</sup>	Length	238.1	5.64	the state
Present work <sup>b</sup>	Length	237.7	5.97	-0.12
Present work c	Length	237.7	5.71	-0.10
Present work <sup>d</sup>	Length	237.8	5.85	-0.12
Haussühl	Ultrasonic	237.3		1.1.1.1
Ghafelehbashi and Koliwad	Ultrasonic	237.0	5.37	
Barsch and Chang	Ultrasonic	234.2	5.39	20
Spetzler et al.	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 et al.	Shock	237.3°	5.50	and in

<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 °C.

°A weighted average for the parameters  $B'_0$  from all equations and  $B''_0$  from all the three-parameter equations at T=29.5and 40.4 °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 °C.

"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  $-0.10\pm0.05$  kbar<sup>-1</sup>. 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 kbar<sup>-1</sup>. 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 <sub>0</sub> (kbar)	B <sub>0</sub> '	B <sub>0</sub> " (kbar <sup>-1</sup> )
238.20 <sup>a</sup>	5.60ª	The West Cana Trilling Diversity of
238.00 <sup>b</sup>	5.75 b	-0.06 <sup>b</sup>
238.00 °	5.53 °	-0.03°

<sup>a</sup>A weighted average of the two-parameter equation at T = 29, 5 °C.

<sup>b</sup>A weighted average of the three-parameter equations at T = 29.5 °C.

°A weighted average for the parameters  $B'_0$  from all equations and  $B''_0$  from all the three-parameter equations at T=29.5and 40.4°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 kbar<sup>-1</sup>. 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 threeparameter 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 bccphase 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 b	Fe transition (kbar)	NaCl transition
ME <sub>1</sub> <sup>b</sup>	59.9	86.2	170	468
BE1b	58.0	81.7	153	362
GGKE b	58.3	82.4	154	356
ME <sub>2</sub> °	52.1	67.5	96	120
BE <sub>2</sub> °	54.9	74.4	121	173
KE c	55.8	76.8	134	271
ME <sub>2</sub> <sup>d</sup>	52.3	68.7	100	132
BE <sub>2</sub> d	54.6	74.3	122	196
KEd	55.4	76.2	132	274
KE e	55.3	75.8	130	262
KE f	54.1	74.0	136	258
Decker	54.7	76.4	136	306
Drickamer		73-75	(110-113)	
Ref. 37	55	77	the standing to	1 the second

<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.

• 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.

barium and bismuth transitions were taken from the data of Jeffery et al.<sup>33</sup>. The data of Mao et al.<sup>34</sup> and Bassett et al. 35 was relied on to estimate the iron and sodium chloride transitions respectively.

It has been generally established<sup>36,37</sup> (if not firmly) that Bi III-V transition is at  $77 \pm 3$  kbar, whereas the two-parameter equations ME<sub>1</sub>, BE<sub>1</sub>, and GGKE predict transition pressures approximately 7-10% higher than the presently accepted values. (Note that ME, predicts the NaCl transition at a pressure nearly twice the actual value; see Sec. VI.) This indicates the inadequacy of the two-parameter equations for  $V/V_0 < 0.9$  suggesting a nonzero negative value for  $B_0^{"}$ . At the same time it implies that the magnitude of  $B_0''$  has to be greater than 0.03 kbar<sup>-1</sup>, because the use of BE, and GGKE assumes an inherent value of -0.03 kbar<sup>-1</sup> in this case. Hence, for NaCl, the three-parameter equations of state should be a better choice over the two-parameter equations of state for  $V/V_0 < 0.9$ .

Just on physical grounds, one can rule out both ME<sub>2</sub> and BE, equations. The use of these equations with  $B_0'' < 0$  leads to a physically and thermodynamically unreasonable condition at high pressures. The bulk modulus increases to a maximum and then decreases and becomes negative. That leaves Keane's equation as the only other alternative of the equations considered here. Anderson<sup>38</sup> has found good agreement between extrapolated ultrsonic data and shock-wave data for many materials on the basis of Keane's equation. Based on the use of Keane's equation, the values obtained for the Ba I-II and Bi III-V transitions are 55.3 and 75.8 kbar, respectively, which is in good agreement with the presently accepted values. 36,37

### **V. IRON TRANSITION**

Based on Keane's equation and using Mao et al.'s<sup>34</sup> x-ray data, the Fe transition is estimated to be 133 kbar. However, this represents the maximum pressure of phase transition. Their experimental data indicates the existence of the hcp phase of Fe (the highpressure phase) as low as 80 kbar (presumably on the way down), thereby indicating extreme sluggishness for the phase transformation in their apparatus. It is generally believed that the Fe transition pressure is lower than that of the lead transition. Takahashi and Bassett<sup>39</sup> estimate 130 kbar for both these transitions. Drickamer's<sup>36</sup> estimate for the Fe transition is 113 kbar and for the lead transition is 132 kbar. Hence it would seem inappropriate to use Mao et al.'s<sup>34</sup> lattice parameter measurements to estimate the Fe transition point; because of sluggishness, such an estimate is likely to be high.

# VI. SODIUM CHLORIDE TRANSITION

As indicated in Table VI, the NaCl transformation is estimated to be approximately 262 kbar. Once again we are using Keane's equation and Bassett et al.'s35 x-ray measurements of the lattice parameter for NaCl. Decker's equation of state gives the transformation to be approximately 306 kbar. Piermarini and Block's estimate is 291 kbar once again based on Decker's equation of state. However, there are reasons to believe that it might be an overestimate. Shock-wave experiments of Fritz et al. indicate that the Hugoniot

pressure for transformation is 231 kbar at approximately 1125 °K. As Fritz et al. mention, the largest uncertainty involved in transforming a Hugoniot to an isotherm comes from the lack of information on the behavior of  $\gamma$  the Grüneisen parameter at these pressures and temperatures. One usually makes the assumption that  $\gamma$  is a function of volume only. In fact Fritz *et al.* make use of the assumption that  $\gamma/V$  is a constant and it is uncertain if such a volume dependence remains accurate to the large volume changes that take place at such high pressures. Second a pressure correction of 70 kbar to the transition pressure for a temperature change of approximately 800 °C seems large compared to other alkali halides<sup>40,41</sup> and iron.<sup>42</sup> In fact for Fe, where presumably the most accurate measurement exists, the pressure correction is only 20 kbar for a temperature change of 550 °C. If Fe is representative of pressure corrections for temperature changes, then for NaCl the correction would be only 30 kbar, which would then put the transition pressure for NaCl at approximately 260 kbar. Furthermore, the shock-wave data also indicates that the (111) direction of NaCl has a lower pressure transition than the (100) direction. Unfortunately there are no measurements for the (111) direction within the Hugoniot range of 212 to 231 kbar to indicate a transition if any. In other words it is quite possible that the transition takes place as low as 213 kbar on the Hugoniot for the (111) direction. Some more experimental points in that region would definitely help clarify the situation.

Piermarini et al.<sup>2</sup> have estimated the transition pressures for GaP and ZnS to be 220 and 150 kbar, respectively, using their ruby fluorescence gauge calibrated against Decker's equation of state for NaCl. This would give a pressure ratio of 1.47 for the two transitions. However, Wanagel and Ruoff<sup>43</sup> have devised a novel technique thereby which they load both the sample GaP and ZnS together in their Bridgman anvil pressure cell and have simultaneously monitored the transitions. The load ratio that they repeatedly obtain for these transitions is 1.3. Hence if one accepts a value of 150 kbar for ZnS, that would indicate that the GaP transition should be approximately 195 kbar based on a linear extrapolation of pressure-load relationship ignoring the loss of efficiency with increasing load. If one includes the loss of efficiency in Bridgman anvil devices it would lower the GaP transition pressure even further. It is quite conceivable that this discrepancy of 25 kbar represents a departure from Decker's equation of state at approximately 200 kbar, and if that is so, one would expect even a larger discrepancy around 300 kbar and a proportional basis would be at least 37 kbar. This would tend to push the NaCl transition down to as low as 254-269 kbar.

# VII. CONCLUSION

The results of the present experiment can be summarized as follows:

(1) The best values of the isothermal bulk modulus and its pressure derivatives at 29.5 °C and at atmospheric pressure are  $B_0 = 237.7 \pm 0.3$  kbar,  $B'_0 = 5.71 \pm 0.25$ , and  $B_0'' = -0.10 \pm 0.05 \text{ kbar}^{-1}$ , respectively.

(2) The isothermal determination of  $B_0''$  represents the first measurement of its kind and the uncertainty associated with its determination is essentially due to the uncertainty in the pressure itself.

(3) Keane's equation of state seems to best represent the present measurements when extrapolated in the highpressure region. The bismuth III-V transition is found to be 75.8 kbar, which is within 1.2 bar of the presently accepted value.

(4) The sodium chloride transition is estimated to be 262 kbar, on the basis of Keane's equation. The main source of error in determining the above transition in addition to questioning (i) the validity of the Keane's equation and (ii) the experimental technique<sup>44</sup> of mixing intimately two different materials to determine the lattice parameters of each, is due to the uncertainty in determining  $B_0''$ .

(5) The main source of error in the present measurements is unfortunately the pressure itself. It is known only to  $1 \times 10^{-4}$  and as Tables IV and V indicate, the uncertainty in pressure leads to different values for  $B'_{0}$ and  $B_0''$ , which in turn would estimate different values for pressure transitions at high pressures. Table V is included in the text to emphasize that in estimating the pressure at high pressures using equations of state, the errors are twofold. One is the validity of the equation of state itself and how closely it approximates the experimental situation. Second, it is also due to the uncertainty associated with not knowing the pressures to the desired accuracy at low pressures.

Obvious ways of minimizing the error obtained in determining  $B_0''$  would be by extending the pressure scale to beyond 7.5 kbar, at the same time improving the accuracy of the pressure scale in this low-pressure region. In fact, if the pressure could be measured to the same accuracy as  $V/V_0$  the present length-measurement system would produce an extremely accurate value of  $B_0''$  without resorting to ultrasonic measurements.

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<sup>1</sup>Akifumi Onodera, Naoto Kaeai, Kozo Ishizaki, and Ian L. Spain, Solid State Commun. 14, 803 (1974).

- <sup>2</sup>G.J. Piermarini and S. Block, Rev. Sci. Instrum. 46, 973 (1975).
- <sup>3</sup>E.A. Perez-Albuerne and H.G. Drickamer, J. Chem. Phys. 43, 1381 (1965).
- <sup>4</sup>D. Lazarus, Phys. Rev. 76, 545 (1949).
- <sup>5</sup>R.A. Bartels and D.E. Schuele, J. Phys. Chem. Solids 26, 537 (1965).
- 6S. Haussühl, Z. Phys. 159, 223 (1960).
- <sup>7</sup>M. Ghafeleshbashi and K.M. Koliwad, J. Appl. Phys. 41, 4010 (1970).
- <sup>8</sup>G.R. Barsch and Z.P. Chang, Phys. Status Solidi 19, 139 (1967).
- <sup>9</sup>H. Spetzler, C.G. Sammis, and R.J. O'Connell, J. Phys. Chem. Solids 33, 1727 (1972).
- <sup>10</sup>P.W. Bridgman, Proc. Am. Acad. Arts Sci. 72, 207 (1938). <sup>11</sup>S.N. Vaidya and G.C. Kennedy, J. Phys. Chem. Solids 32, 951 (1971).
- <sup>12</sup>J.N. Fritz, S.P. Marsh, W.J. Carter, and R.G. McQueen in Accurate Characterization of the High Pressure Environment, NBS Special Publication 326, edited by E.C. Lloyd (U.S. GPO, Washington, D.C., 1971), p. 201.
- <sup>13</sup>J.C. Jamieson, Science 139, 1291 (1963).
- <sup>14</sup>D. L. Decker, J. Appl. Phys. 36, 157 (1965).
   <sup>15</sup>D. L. Decker, J. Appl. Phys. 42, 3239 (1971).
- <sup>16</sup>G.J. Piermarini, S. Block, J.D. Barnett, and R.A. Forman, J. Appl. Phys. 46, 2774 (1975).
- <sup>17</sup>J. Scott Weaver, in Ref. 12, p. 325
- <sup>18</sup>W.C. Overton, Jr., J. Chem. Phys. 37, 116 (1962).
- <sup>19</sup>R.C. Lincoln and A.L. Ruoff, Rev. Sci. Instrum. 44, 1239 (1973).
- <sup>20</sup>A. L. Ruoff, R. C. Lincoln, and Y. C. Chen, J. Phys. D 6, 1295 (1973)
- <sup>21</sup>K. Y. Kim, R.E. Terry, and A. L. Ruoff, Rev. Sci. Instrum. 47, 636 (1976).
- <sup>22</sup>F.D. Murnaghan, Finite Deformation of an Elastic Solid (Dover, New York, 1967).
- <sup>23</sup>F. Birch, Phys. Rev. 71, 809 (1947).
- <sup>24</sup>F. Birch, J. Geophys. Res. 57, 227 (1952).
- <sup>25</sup>A. Keane, Aust. J. Phys. 7, 322 (1954).
- <sup>26</sup>R. Grover, I.C. Getting and G.C. Kennedy, Phys. Rev. B 7, 567 (1973)
- <sup>27</sup>K. Y. Kim, L.C. Chhabildas, and A.L. Ruoff, J. Appl. Phys. 47, 2862 (1976).
- <sup>28</sup>A.K. Singh and G.C. Kennedy, J. Appl. Phys. 45, 4686 (1974).
- <sup>29</sup>A. L. Ruoff, J. Appl. Phys. 46, 1389 (1975).
- <sup>30</sup>G. L. Kinsland and W. A. Bassett, Rev. Sci. Instrum. 47,
- 130 (1976).
- <sup>31</sup>P.L. Heydemann (private communication). <sup>32</sup>A. L. Ruoff, R.C. Lincoln, and Y.C. Chen, Appl. Phys.
- Lett. 22, 310 (1973). <sup>33</sup>R.N. Jeffery, J.D. Barnett, H.B. Vanfleet, and H.T. Hall,
- J. Appl. Phys. 37, 3172 (1966). <sup>34</sup>Ho-Kwang Mao, W.A. Bassett, and T. Takahashi, J. Appl.
- Phys. 38, 272 (1967).
- <sup>35</sup>W.A. Bassett, T. Takahashi, H.K. Mao, and J.S. Weaver, J. Appl. Phys. 39, 319 (1968).
- 36H.G. Drickamer, Rev. Sci. Instrum. 41, 1607 (1970). <sup>37</sup>See Ref. 12, p. 313.
- <sup>38</sup>O. L. Anderson, Phys. Earth Planet Inter. 1, 169 (1968).
- <sup>39</sup>T. Takahashi, H.K. Mao, W.A. Bassett, Science 165, 1352 (1969).
- 40C. W. F. T. Pistorious, J. Phys. Chem. Solids 25, 1477 (1964).
- <sup>41</sup>C.W.F.T. Pistorious, J. Phys. Chem. Solids 26, 1003 (1965).
- <sup>42</sup>H. M. Strong and F. P. Bundy in Ref. 12, p.238.