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^{-1}, 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 [1] has now been scaled down to approximately 200 kbar.[2] 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,[3] ultrasonic data,[4–9] static-compression data,[10,11] and shock-wave data,[12] NaCl has emerged as a strong candidate for use as a pressure gauge.

Jamieson[13] first used NaCl as an internal pressure standard in his x-ray apparatus. Since then Decker[14,15] has calculated a Mie-Grüneisen equation of state for NaCl based on the Born-Mayer potential. Piermarini *et al.*[16] 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[4–8] yield a value of 5.35 for B'_0, whereas the static-compression data of Bridgman[10] and Vaidya and Kennedy[11] give 4.61 and 4.92, respectively. From the shock-wave data[12] 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[12,17] 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.[18] 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,[19] as it is capable of measuring V/V_0 to a precision of 1×10^{-7}. Admittedly by doing ultrasonic measurements one is indeed a pressure derivative ahead when compared to length measurements.[20] 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[21] 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

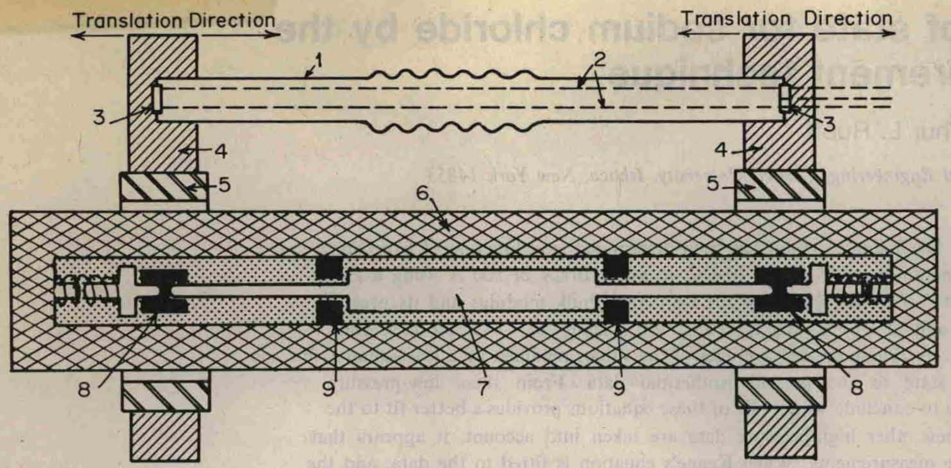

FIG. 1. Schematic of length-measurements system: (a) laser path vacuum bellows; (2) laser beam; (3) interferometer mirrors; (4) coupling plates; (5) LVDT's (6) pressure vessel; (7) specimen; (8) magnetic cores; (9) ball bushings.

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 10^4 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 1×10^{-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.[20]

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: $p=P-P_0$, $\eta=B_0'$, $\psi=B_0B_0''$, $Z=p/B_0$, and $x=V_0/V$. Note that η, ψ, 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_1 is the only equation of state in that list for which B_0'' identically equals zero. The expressions for BE_1 and GGKE do not explicitly contain the parameter B_0''. The appropriate expression was used[27] 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