

## Compression of NaCl and CsCl to 32 kbar\*

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The compression of NaCl and CsCl has been measured to 32 kbar using time-of-flight neutron-diffraction techniques. These measurements indicate that Decker's equation of state for CsCl yields pressures which are about 2% lower than does his equation of state for NaCl over this range of pressures.

Recently, Decker<sup>1</sup> calculated equations of state for NaCl and CsCl using the same theoretical approach for each. He proposed that the consistency of this calculation could be checked by simultaneously measuring the volume of these materials while they were subjected to the same pressures and temperatures. No such direct measurement has been reported in the literature; so while calibrating our high-pressure time-of-flight neutron diffractometer we decided to compare these two materials at several pressures up to 32 kbar at room temperature. Since many laboratories use the NaCl equation of state as their pressure standard, an experimental consistency check is important to the problem of pressure measurement.

The experiment consists of simultaneously measuring the lattice parameter of CsCl and NaCl in a given high-pressure environment and then using Decker's equations of state to calculate the pressures,  $P_{\text{NaCl}}$  and  $P_{\text{CsCl}}$ , within the pressure cell. Differences between  $P_{\text{NaCl}}$  and  $P_{\text{CsCl}}$  can be used to indicate weaknesses of the theoretical equations of state, or to indicate inaccuracies in the parameters used in the theory.

Two sets of high-pressure measurements were made. In the first, the sample consisted of alternate 0.56-cm-diam pellets of NaCl and CsCl, the former being 0.32 cm long and the latter 0.58 cm long. These pellets were wrapped in a sleeve of 0.025-cm-thick lead forming a cylinder 3.92 cm in length. This sample was loaded in an  $\text{Al}_2\text{O}_3$  pressure cell, which has been described in earlier publications,<sup>2,3</sup> with 0.32-cm-long plugs of Teflon at either end. The sample for the second set of measurements consisted of a mixture of fine powders of CsCl and NaCl in the ratio 3 to 1 by weight. These powders were also compressed into pellets and loaded as discussed above. The NaCl and CsCl powders were ultrapure salts with less than 40 ppm impurities purchased from Alfa Inorganics. The powders were kept in a drying oven at 125 °C for several days prior to forming the pellets.

The pressure cell is a double-acting piston-cylinder apparatus whose capabilities are discussed in detail elsewhere.<sup>2,3</sup> The neutron beam from the CP-5 facility at Argonne is about 2.5 cm high by 0.6 cm wide at the sample and time-of-flight diffraction patterns were accumulated at scattering angles of 30° and 60° from the forward beam. The collimation of the neutron beam is not perfect and it is possible to distinguish some of the most intense peaks of  $\text{Al}_2\text{O}_3$  and lead in the diffraction pattern, particularly at the 30° scattering angle.

Measurements were made at several difference pressures between 8 and 32 kbar and compared with the zero-pressure pattern. Each pattern was accumulated over a time of one to two days. The time-of-flight neutron-diffraction spectra were piecewise fitted using a PDP-9

computer to a mathematical expression containing up to four Gaussian curves on a linear-ramp background. The results of the least-squares fit gave the  $d$ -spacing for each diffraction peak along with its integrated intensity and the amount of background under the peak. The value of the mean deviation for each of these parameters was also calculated. Prior to the data-taking scans the time-of-flight spectrometer was calibrated by measuring the diffraction patterns of Ge and Si. From plane-spacing measurements at each pressure the fractional change in the lattice parameter from the zero-pressure value was determined for each salt. This change was used in conjunction with Decker's equation of state to determine the pressures  $P_{\text{NaCl}}$  and  $P_{\text{CsCl}}$ .

Figure 1 displays a portion of the diffraction patterns for plane spacings between 1.75 and 3.50 Å for the 60° counters at 0 and 29 kbar from the second sample. The diffraction pattern for  $d$ -spacings down to 1.0 Å was measured but not used in the analysis because there were too many unresolved lines in this region. Unfortunately, the lattice parameters of NaCl and CsCl are such as to cause many of the diffraction peaks to overlap in this region. The lattice parameters of NaCl and CsCl at atmospheric pressure were measured to be  $5.6388 \pm 0.0017$  Å and  $4.1197 \pm 0.0011$  Å, respectively, at 23 °C. These values compare very favorably with the literature values of 5.6396<sup>4</sup> and 4.121 Å,<sup>5</sup> respectively. Figure 2 is a graph of the difference in calculated pressures ( $P_{\text{CsCl}} - P_{\text{NaCl}}$ ) vs the NaCl pressure. The round points correspond to the first sample and the diamond-shaped points to the second sample. Only the 60° scattering angle was used on the first run, but the second run is an average of 60° and 30° data.

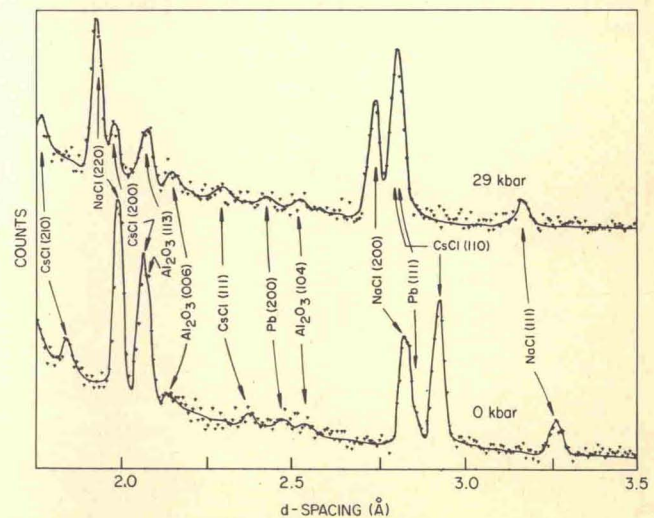


FIG. 1. The neutron time-of-flight diffraction pattern for NaCl and CsCl in the high-pressure cell at 0 and 29 kbar.

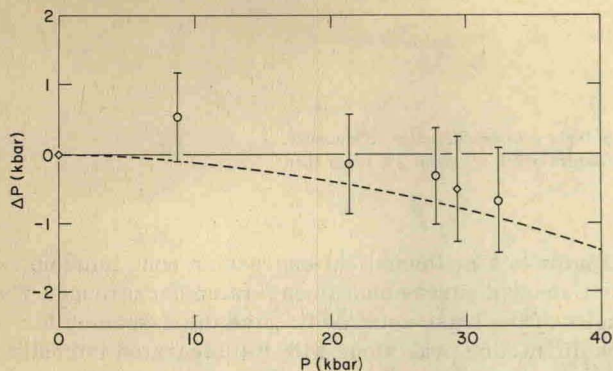


FIG. 2. The differences in the pressures calculated from the equations of state for CsCl and NaCl as a function of the NaCl pressure. The plotting symbols are explained in the text. The dashed curve shows the difference in pressure calculated from Decker's equation of state for CsCl and the pressure calculated from Birch's second-order ultrasonic equation.

The results of this experiment indicate that the pressure calculated from the CsCl equation of state is less than that of NaCl by 0.7 kbar at 30 kbar. The size of the uncertainty in this measurement is about the same size as this difference and yet this difference is likely real because of the agreement in the two separate measurements. The separate compression measurements of NaCl and CsCl by Vaidya and Kennedy<sup>6</sup> and by Bridgman<sup>7</sup> also show this same trend when compared with the calculated equations of state, i. e., -0.5 and -0.2 kbar discrepancy, respectively, at 30 kbar.<sup>1</sup>

In spite of the fact that the pressure from the CsCl equation of state is likely less than that for the NaCl equation of state, this difference does not furnish clear evidence of a difficulty in the theory because the theoretical results are dependent upon certain input parameters, such as the compressibility and the volume dependence of the Gruneisen parameter. Due to the uncertainty in these input parameters, the uncertainties in the pressure calculated from the equations of state of NaCl and CsCl are 0.3 and 0.7 kbar, respectively, at 30 kbar. Thus the uncertainty in the CsCl equation of state alone could lead to the kind of differences observed.

Barsch and Chang<sup>8</sup> have proposed a Birch second-order empirical equation for CsCl where the three parameters, the isothermal bulk modulus and its first and second pressure derivatives, have been measured ultrasonically. Using the ultrasonic parameters they quoted, this equation is

$$P = 251.1(1/x^2 - 1)[1 + 1.49(1/x^2 - 1) + 1.03(1/x^2 - 1)^2]x^{-5}, \quad (1)$$

where  $x = r/r_0$ , with  $r$  as the lattice parameter. In Fig. 2 the dashed curve indicates the difference between the equation of state by Decker and this ultrasonic equation for CsCl. Decker's equation gives a slightly lower pressure than the ultrasonic equation. The pressure from this ultrasonic equation for CsCl agrees somewhat better with Decker's equation of state for NaCl over this pressure range than with the equation of state for CsCl.

There are some applications where one might prefer to use CsCl rather than NaCl as a pressure calibrant. It is more compressible than NaCl and gives an indication of the pressure with a somewhat better precision than NaCl does in this pressure range. We suggest that if one should use this material they should increase the pressure calculated by Decker's equation of state by about 2% for pressures up to 30 kbar. It would be interesting to extend this measurement to much higher pressures where the differences in  $P_{\text{CsCl}}$  and  $P_{\text{NaCl}}$  might be more pronounced.

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