

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

It has been generally established^{36,37} (if not firmly) that Bi III-V transition is at 77 ± 3 kbar, whereas the two-parameter equations ME_1 , BE_1 , and GGKE predict transition pressures approximately 7–10% higher than the presently accepted values. (Note that ME_1 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^{-1} , because the use of BE_1 and GGKE assumes an inherent value of -0.03 kbar^{-1} 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_2 and BE_2 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. Anderson³⁸ has found good agreement between extrapolated ultrasonic 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.*'s³⁴ 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 high-pressure 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 Bassett³⁹ estimate 130 kbar for both these transitions. Drickamer's³⁶ 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.*'s³⁴ 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 γ the Grüneisen parameter at these pressures and temperatures. One usually makes the assumption that γ is a function of volume only. In fact Fritz *et al.* make use of the assumption that γ/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^{40,41} and iron.⁴² 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.*² 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 Ruoff⁴³ have devised a novel technique whereby 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 $B_0 = 237.7 \pm 0.3 \text{ kbar}$, $B_0' = 5.71 \pm 0.25$, 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 high-pressure 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 technique⁴⁴ 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 1×10^{-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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