

$$B_T = B_0 + nP = B_0(V_0/V)^n \quad (3b)$$

and

$$P = B_0/n[(V_0/V)^n - 1] \quad (3c)$$

and the Tait equation[29, 30];

$$-(\partial P/\partial V)_T = J^{-1}(L + P). \quad (4)$$

MacDonald has discussed the application of curve-fitting techniques to these equations for representing experimental data and their relative suitability for this purpose[29]. He stresses that neither of these equations has any firm theoretical basis and each must be treated as a heuristic relationship which must be used with caution for extrapolation. Our experience has been that no experimental data are sufficiently precise so that a judgement can be made as to which of equations (1), (3) or (4) is 'correct.' Certainly, the power series representation of  $\Delta V/V_0$  in terms of pressure as used by Bridgman for small compressions [31] and in the representation of earlier sodium data[9] is quite unsatisfactory.

The most convenient representation of our final equation of state is in terms of equations (3) since both  $B_T$  and  $(\partial B_T/\partial P)_T$  are in principle readily obtainable from ultrasonic data [26]. Equation (3c) is difficult to use when the absolute length of the sample can be obtained only by extrapolation, as in our experiments. The aesthetically displeasing procedure which was used to analyze our equation of state data involves using the Birch function fits to the individual isotherms (equation (1)) to obtain both pressures and bulk moduli as a function of temperature for fixed values of the volume and then to obtain the coefficients for equation (3) from a plot of these quantities (see below). This experiment involves systematic errors which cannot be evaluated (uncertainties in the friction correction, variation of the sample holder diameter with pressure and temperature, etc.) and which internal inconsistencies suggest introduce errors of the order of 0.5–1 per cent of the total compression. These are large when compared with the

errors involved in the method of analysis. The final objective only can be to reproduce the data (to within an estimated experimental accuracy) using an equation of state which contains 'reasonable' parameters. Because of the uncertainties in the systematic errors, precise extrapolations of this equation of state are risky.

#### EXPERIMENTAL RESULTS

Figure 1 summarizes the experimental  $P$ - $V$ - $T$  results obtained for our two samples. The actual data [ $L(T, P)/L_0(273^\circ\text{K}, P = 0)$ ] have been converted to molar volumes by assuming the molar volume at  $273^\circ\text{K}$  and atmospheric pressure to be  $70.00 \text{ cm}^3$ [32, 33]. The use of data points on this plot is misleading. The actual data consist of a series of  $P$ - $V$  isotherms, each of which has been graphically smoothed twice (before and after making the friction correction) before subtracting a smooth 'background' or sample holder distortion correction. The 'experimental points' have been read from the smooth isotherms at the specified pressures and are useful to show differences between the isotherms. The solid lines are calculated from an analytical equation of state which will be described in the next section.

The results for both samples and the calculated equation of state are in excellent agreement from 2 to 14 kbar (with maximum deviations of the order of  $0.2 \text{ cm}^3/\text{mole}$ ). However, differences of up to twice this amount appear at the lowest temperatures and the highest pressures when the calculated and experimental values are compared. This effect is shown in Fig. 2 where the room temperature and absolute zero isotherms are plotted as calculated from our analytical relationship (full line) and as observed for the small sample holder (dashed line). In particular, the results suggest that the thermal expansion is approximately zero at 20 kbar. The deviation between the calculated curve and the experimental results indicates that the low temperature small sample holder data deviate

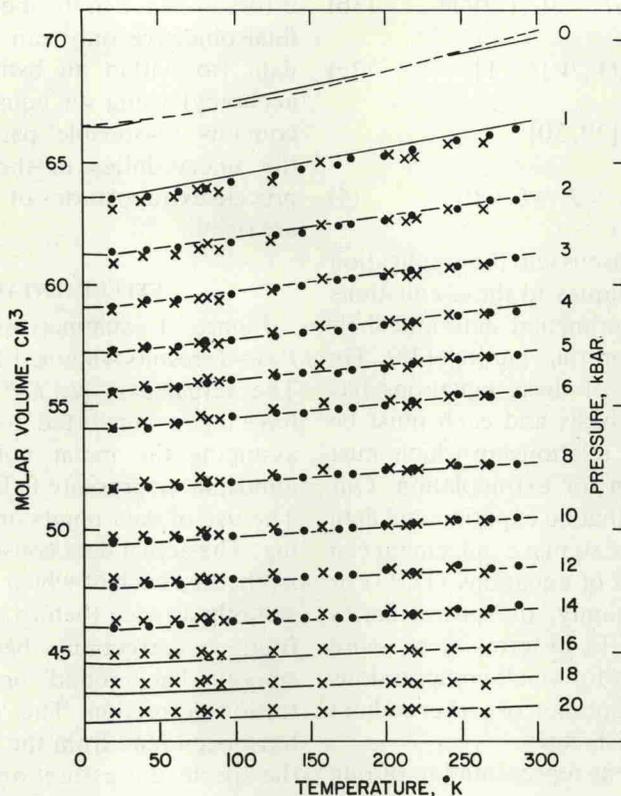


Fig. 1. The experimental equation of state for cesium metal. The 'experimental points' which are indicated have been read off the smoothed experimental isotherms at equal pressure increments, and indicate only the relative consistency of the various isotherms.

appreciably from both equations (1) and (3), and this is evident in our data analysis in the form of systematic deviations. The small sample holder (high pressure) data are not as smooth and are perhaps less reliable (for unknown reasons) than the large sample holder data on which our equation of state is based. Compressions as calculated from this equation of state may be in error at 20°K and 20 kbar by as much as 2 per cent; this results in an error in the molar volume at this temperature and pressure of less than 1 per cent. Because of this ambiguity, the following discussion will be applicable almost completely to pressures less than 14 kbar or molar volumes greater than 46 cm<sup>3</sup>.

The present data can be compared directly with earlier 10,000 atm, 4°K data [22], with Bridgman's room temperature data to 40,000 kg/cm<sup>2</sup> [15, 16] and with the X-ray data of Hall *et al.* [18]. The 10,000 atm, 4°K data give compressions which are too low by approximately 4 per cent at all pressures. The reason for this discrepancy is not known, but the present data are to be preferred because of the refinements in techniques which have been used in the current experiments. Bridgman's two sets of room temperature compression data [15, 16] disagree by 10 per cent at 20,000 kg/cm<sup>2</sup> ( $\Delta V/V_0 = 0.372$  and  $0.344$ , respectively). The corresponding compression for the present results is 0.387. Bridgman's data were