

the pressure scale is the sluggishness of the phase transition. Takahashi, et al. (1968) report that at room temperature the high-pressure phase appears at 127 kbar, that the low-pressure phase persists to a pressure of 152 kbar with increasing pressure, and that the high-pressure phase persists to 83 kbar with decreasing pressure. Stark and Jura (1964) found that short thermal pulses to a sample of iron at pressures above  $118 \pm 6$  kbar would drive the transition towards the high-pressure phase while thermal pulses to an iron sample at pressures below  $118 \pm 6$  kbar would drive the transition towards the low-pressure phase.

TABLE 9. Tin I-II transition at 25 °C

Researcher	Transition pressure (kbar)	Error (kbar)	Method of detection
Stager, Balchan, and Drickamer (1962)	(c) 113-115		Electrical resistance
Barnett, et al. (1966)	(c) 92	3	X-ray diffraction and electrical resistance
Barnett, revised (1968) <sup>a</sup>	(c) 94	4	
Stark and Jura (1964)	(c) 99	6	Electrical resistance

(c) compression.

<sup>a</sup>Based on NaCl compression data of Barnett, et al. (1966); pressure obtained from Decker's (1971) revised equation of state for NaCl.

Considerable caution should be exercised in the use of iron as a fixed point for pressure calibration. The sluggishness of its transition appears to make it time-dependent, temperature-dependent, and possibly even stress-dependent. As yet, the thermodynamic transition pressure at room temperature has not been adequately established.

#### c. Barium II-III

The high barium transition has been determined only by electrical resistance methods by Balchan and

Drickamer (1961). The pressure calibration was based on the Ba I-II point at 59 kbar to 144 kbar where a resistance increase of 42 percent was observed. This value is the average of four determinations, all on the compression cycle. The reported value of 144 kbar for the Ba II-III transition is undoubtedly high in view of the more recent values for the Ba I-II and Bi III-V transitions. Further calibration work needs to be done.

TABLE 11. Barium II-III transition at 25 °C

Researcher	Transition pressure (kbar)	Method of detection
Balchan and Drickamer (1961).....	144	Electrical resistance.

#### d. Lead

The phase transition in lead has been suggested as a calibration point (Drickamer, 1963). Balchan and Drickamer (1961) reported a pressure of 161 kbar for the transition in lead, basing their measurements on an extrapolation from fixed points below 100 kbar (Ba I-II, 59 kbar; Bi III-V, 90 kbar). Subsequently, the lead transition has been used by several workers as a calibration point at 161 kbar.

Takahashi, et al. (1969) found that in the diamond-anvil x-ray press, the high-pressure phase of lead (hexagonal close-packing) appears at  $130 \pm 10$  kbar with increasing pressure at room temperature. This value was based upon the lattice parameter of iron mixed with the lead to serve as a pressure calibrant. The iron compression data used for this purpose are those of Takahashi, et al. (1968), who based their measurements upon an NaCl scale that does not differ significantly from that of Decker (1968). NaCl was not used directly with lead because of a chemical reaction between the two. Vereshchagin, et al. (1969), using a supported Bridgman anvil apparatus similar to the Drickamer cell, found that

TABLE 10. Iron  $\alpha$ - $\epsilon$  transition

Researcher	Transition pressure (kbar)	Temp.	Method of detection	Remarks
Bancroft, et al. (1956)	130		Shock	
Bancroft, et al. (1956)	128		Shock	Corrected to hydrostat.
Balchan and Drickamer (1961)	$133 \pm 2$	20 °C	Electrical resistance	Bridgman anvils. Increasing load.
Takahashi and Bassett (1964)	130	(R.T.)	X-ray diff.	Represents maximum pressure. First observed $\epsilon$ with increasing load.
			Diamond cell	
Stark and Jura (1964)	$118 \pm 6$	(R.T.)	Electrical resistance	Transition driven by short thermal pulses. Resistance measured at R.T.
Loree, et al. (1966)	$127 \pm 1$		Shock	Corrected to hydrostat.
Takahashi, et al. (1968)	127	23 °C	X-ray diff.	Represents maximum pressure. First observed $\epsilon$ with increasing load.
			Diamond cell	
Takahashi, et al. (1968)	83	23 °C	X-ray diff.	Represents minimum pressure. Last appearance of $\epsilon$ with decreasing load.
			Diamond cell	
Takahashi (unpublished)	$125 \pm 10$	23 °C	Electrical resistance	Calibration based on extrapolation from fixed points (Jeffery, et al. 1966) using Decker's revised NaCl scale.
			Drickamer cell	

iron showed a resistance jump at a load slightly less than that of lead. Although they interpreted this as indicating that the iron transition should be revised to a higher pressure to conform with the lead transition, there is evidence that the pressure of the lead transition should be revised downward to be consistent with the iron transition. They calibrated their device assuming the following pressures for transitions on the fixed point scale: Bi I-II (24.5 kbar), Bi III-V (88 kbar), and Pb I-II (161 kbar). These calibration points are based on linear extrapolation of a pressure-load relationship established at lower pressures by force/area calculations and are subject to error by loss of efficiency with increasing load.

The loss of efficiency in Bridgman anvil devices can be attributed to two factors: (1) the compressibility and amount of extrusion of the gasket material decrease with increasing pressure, and (2) deformation of the anvils causes a decrease in the ratio of maximum pressure to applied pressure. The latter has been observed to take place in diamond anvils. Since the anvils employed by Bridgman (1940b, 1942, 1952), Balchan and Drickamer (1961), and Vereshchagin, et al. (1969) are larger than the diamond anvils and are constructed of tungsten carbide, they probably deform more and at lower pressures than the diamond anvils. This deformation results in a greater loss of efficiency at pressures above 100 kbar. Recent work by Vereshchagin (verbal communication) indicates that he feels that the pressures for the transitions in iron and lead should be revised downward. His new values are more consistent with those based on x-ray diffraction (Takahashi, et al., 1969; Mao, et al., 1969).

In light of the discrepancies for the lead transition pressure, we recommend caution in the use of lead as a fixed point on the pressure scale. In addition, we feel that further investigations on the subject should be made.

Recent results by Drickamer (1970) and Vereshchagin, et al., (1970) on calibration in the higher pressure range are of particular interest to this report. Drickamer gives the transition pressures Bi(III-V)=73-75 kbar, Fe( $\alpha$ - $\epsilon$ )=110-113 kbar, Pb=128-132 kbar, Ba=118-122 kbar, while the values of Vereshchagin, et al. are Bi(III-V)=79 kbar, Fe( $\alpha$ - $\epsilon$ )=129 kbar, Pb=138 kbar, and Ba=125 kbar.

#### 4. Interpolation and Extrapolation Methods and Their Calibration

Once a set of fixed points has been chosen it is then necessary to devise manometers to measure pressure at intermediate points. There are many pressure gages which have been used for this purpose, several of which will be discussed in this section. It is also desirable to consider systems for determining pressures above that at which one can measure the pressure in a fundamental way since our present capabilities allow us to generate pressures in excess of our ability to accurately measure

TABLE 12. Lead I-II transition at 25 °C

Researcher	Transition pressure	Method of detection
Balchan and Drickamer (1961).	161 kbar.....	Electrical Resistance.
Takahashi, et al. (1969), Mao, et al. (1969).	130 ± 10 kbar.	X-ray Diffraction.

them. Thus, we will also consider extrapolation techniques in this chapter.

#### 4.1. Theoretical Equations of State

There are many uses of equations of state in high pressure calibration, the most prominent of which are as interpolation and extrapolation formulas. They are also useful in determining pressure changes due to temperature differences, and also possibly even to aid in establishing a high pressure scale. Temperature effects will be mentioned both here and in section 6.

##### a. Proposed Isothermal Equations

There are several types of interpolation equations relating pressure and volume along a given isotherm, the simplest of which is a simple power series

$$V/V_0 = 1 - aP + bP^2 + \dots \quad (1)$$

This is the form in which Bridgman (1958) represented his results and is called the Bridgman equation. The next step involves semi-empirical equations which have been derived using certain approximations. The most common of these are the Murnaghan equation (Murnaghan, 1944),

$$P = \frac{B_0}{k} [y^{3k} - 1] \quad (2)$$

the Birch equations (Birch, 1947)

$$P = 3 \frac{B_0}{2} (y^7 - y^5) \quad (3)$$

and

$$P = \frac{3B_0}{2} (y^7 - y^5) [1 - \xi(y^2 - 1)] \quad (4)$$

and the Tait equation (Tait, 1898)

$$V/V_0 = 1 - \frac{\ln\left(1 + \frac{rP}{B_0}\right)}{r} \quad (5)$$

There are also various modifications of these equations.

In the above equations,  $B_0$  is the initial bulk modulus at atmospheric pressure,  $y = (V_0/V)^{1/3}$  where  $V_0$  is the