have shown that the equilibrium pressure is located near the upper part of the nucleation hysteresis for the Bi I–II transition, and since all work previous to Heydemann took the center of some hysteresis interval and Heydemann measured the equilibrium pressure, Heydemann's value would be higher but correct.

3.4. Fixed Points Between 30 and 80 Kbar

In a quest for higher pressures Bridgman developed a supported piston-cylinder system capable of 50-kbar pressure and later a two-stage piston-cylinder system capable of 100-kbar pressure (Bridgman 1935, 1941). The 100-kbar apparatus was essentially a $^{1}/_{16}$ inch diameter piston-cylinder assembly totally immersed in a larger piston-cylinder liquid-containing vessel operating at pressures of 25 to 30 kbar. The piston material was tungsten carbide, which had a compressive strength of 45 kbar at one bar. The compressive strength increases due to the confining pressure and allows pressures of over 100 kbar to be reached.

Using this two-stage apparatus Bridgman (1942, 1945, 1948) measured the compression ($\Delta V/V_0$) of numerous solids to 100 kbar. Many phase transformations were indicated by discontinuities in the volume at specific indicated pressures. Such routinely measured transitions were not intended as fixed points but as exploratory work. Later workers began to use transitions in Tl, Cs, Ba, and Bi reported by Bridgman at 40,000 kg/cm^2 (39 kbar), 45,000 kg/cm^2 (44 kbar), 60,000 kg/cm^2 (59 kbar), and 90,000 kg/cm^2 (88 kbar) as fixed-point calibration values as discussed below.

Using a different technique, Bridgman (1952) measured the electrical resistance on many metals and alloys to reported pressures of 100 kbar. The apparatus employed two opposed anvils with truncated ends press-fitted into steel support rings, and is commonly known as Bridgman anvils. The sample was encased in silver chloride surrounded by a 0.010-inch thick ring of pipestone, all of which was compressed between the flat center portion of the anvils. Pressure in the anvil apparatus was determined from the ratio of the applied force to the area of the anvil with no regard to pressure gradients. The method of pressure determination was assumed valid due to correlation of the observation of the known bismuth transition at 25 kbar.

Determining pressures in this manner, Bridgman reported electrical-resistance measurements on many metals and alloys, a number of which showed discontinuities indicating phase transformations. Transitions in Tl, Cs, and Ba were reported at 45,000 kg/cm^2 (44 kbar), 54,950 kg/cm^2 (54 kbar), and 80,000 kg/cm^2 (78 kbar) respectively, but no transition was reported in bismuth above the Bi II–III transition. The study was intended as a routine exploratory resistance study of a large number of materials. Bridgman (1952) assumed that the transitions indicated by volume change and by resistance were manifestations of the same transformations and was not surprised at the pressure discrepancies. He attributed the lack of detection of the higher Bi transition in the resistance study to a negligibly small change in resistance. Later, as other workers began using these transitions to establish pressures, a great deal of discussion was generated as to whether the volume and resistance measurements actually indicated different transformations.

Since electrical resistance discontinuities were relatively easy to measure in the solid-media systems such as the "belt" and the multi-anvil devices made popular by the diamond synthesis, Bridgman's resistance transition pressures were used as fixed points, and a so-called "resistance scale" came into general use. It is apparent from Bridgman's writing that neither his volume measurements nor his electrical resistance measurements were intended as calibration experiments, but it is also obvious that the volume measurements were made with much greater care.

Bundy (1958) did measure an electrical transition in Bi at very high pressures. Using an extrapolation of a load vs pressure curve for the belt apparatus in which pressures were determined using the Bridgman resistance scale, Bundy placed the high-pressure Bi transition at 122.5 kbar.

By 1961 it became apparent to the scientific high-pressure community that the pressure calibration above 25 kbar was very uncertain and that the points being used as fixed points had never been well-characterized. Bridgman's volume measurements were generally accepted as more accurate than the resistance measurements, and reference was often made to Bridgman's "volume scale." One confusing item in the literature requires clarification. Bridgman in his volume measurements on bismuth reported five (5) discontinuities below 100 kbar. As a result eight (8) phases were designated on tentative phase diagrams for Bi. The high-pressure transition measured by electrical resistance was designated as the V–VIII transition and was so referred to in the literature of the early sixties. More recent work has failed to confirm two of the volume discontinuities, and this transition is now designated as the III–IV transition.

Vereshchagin, et al. (1966) have reported calibration pressures for several transitions in the 30 to 100 kbar range. They claim the use of a "free-piston gage to 100 kbar", but the description of the apparatus is so meager that no meaningful evaluation can be made. From the description given it is obvious that the use of the term "free-piston gage" is out of order, and the stated accuracy of the measurements is questionable.

a. Thallium

The earliest work dealing with the Tl II–III transition pressure was that of Bridgman (1935, 1941). His first published value of 41,000 kg/cm^2 (40 kbar) was the result of routine volumetric measurements in which it was noted that the "band of indifference" was fairly wide. His next published value for the Tl II–III transition pressure was

45,000 kg/cm² (44 kbar) in the electrical resistance study mentioned. This value was obtained on the increasing pressure cycle, and apparently no attempt was made to find an equilibrium pressure as appears to be the case in the volumetric study. In this 1935 work, ΔV determinations were obscured by plastic yield of the pressure cylinder in the region of the transition pressure. It is also interesting to note that Bridgman examined shear stress in a large number of materials and reported a transition at a mean pressure of 25,000 kg/cm² (24.5 kbar) in thallium.

Boyd and England (1960) made the first thallium "calibration"-type measurement in a piston-cylinder device of the Coes-Hall design. It could be operated up to 50 kbar and 1750 °C. These authors initially found a total hysteresis of about 11.6 percent between the increasing and decreasing pressure cycles. By cycling about the transition so phases II and III were both present, it was possible to reduce the hysteresis. The author did not state how much this region was decreased. The equilibrium transition pressure was taken as the midpoint of this region. Corrections made for the frictional components gave an average transition pressure of 37.1±3 kbar at 30 °C. The transition was detected by the electrical resistance discontinuity of thallium which was enclosed in silver chloride. The frictional effects were a result of piston friction as well as reversible effects in the pressure environment.

The next determinations on the Tl II–III point were those of Kennedy and LaMori (1961 and 1962) using a piston-cylinder device in which the piston could be rotated slightly in order to reduce frictional effects. It would be difficult to analyze the actual effect of this rotation since according to a comment by F. Dachille "only a few (couple of) *very* short strokes were used at each pause in the running of the transition . . ." The piston was not completely free to rotate as in the free-piston gage. In both the above cited studies the equilibrium transition pressure was reported to be 36.69±0.1 kbar. The error flag represents repeatability and does not reflect systematic errors. It is felt that the uncertainty of Kennedy and LaMori (1961, 1962) does not adequately reflect an appraisal of possible errors; thus, an error flag of ±0.5 kbar has been assigned to this work. Vereshchagin, et al. (1966) reported a value of 39.9±0.4 kbar using their so-called "free-piston" gage. The "best value" cited in table 5 for the transition pressure of the Tl II–III transition is 36.7±0.5 kbar. This value represents a weighted average of the studies by Boyd and England with the study by Kennedy and LaMori. Bridgman's work on thallium does not represent an attempt to calibrate this point, and Vereshchagin, et al. give insufficient detail to evaluate their work. The error flag is the estimate of the reviewers of the error in the Kennedy and LaMori study.

b. Cesium

The Cs I–II transition was first detected by Bridgman (1938b) by electrical resistance methods using an improved modification of his 50 kbar apparatus. He noted that the transition was very rapid and had little hysteresis. In a later measurement by volume methods, this same fact was noted, but the transition pressure was determined to be 23,000 kg/cm² (22.5 kbar, Bridgman, 1938a).

Kennedy and LaMori (1961, 1962) made the only other calibration study of this point and placed the transition at 22.6±0.6 kbar at 25 °C.

The second transition in cesium was first reported by Bridgman (1949) at 45,000 kg/cm² (44 kbar) as a part of the series of volumetric measurements. Later Bridgman (1952) measured a sharp "cusp"-type peak in the electrical resistance which he reported at 54,950 kg/cm² (54 kbar). The shape of this resistance curve caused Bridgman and others a great deal of concern since there was no discontinuity present. This transition was referred to as the cesium II–III transition and used as a fixed point value. Work by Hall, Merrill, and Barnett (1964) has shown that there are actually two closely spaced transitions associated with this point, i.e., Cs II–III and Cs III–IV. These transitions are separated by about 0.5 kbar, and both are sharp discontinuities in resistance. Through simultaneous monitoring of electrical resistance and x-ray diffraction measurements,

TABLE 5. Thallium II–III transition

Researcher	Transition pressure (kbar)	Error (kbar)	Temp.	Method of detection	Sample purity
Bridgman (1935)	(e) 40		30 °C	Volume	Highly purified
Bridgman (1952)	(c) 44		Room temp.	Resistance	Highly purified
Boyd and England (1960)[a]	(e) 37.1	3	29±1 °C	Volume	99.99% Electrolytic
Kennedy and LaMori (1961)[a]	(e) 36.69	See text	25 °C	Volume	99.95%
Kennedy and LaMori (1962)[a]	(e) 36.69	See text	25 °C	Volume	99.95%
Vereshchagin, et al. (1966)	36.9	0.4			
Best Value	36.7	0.5	25 °C		

(e) equilibrium; (c) compression.
[a] Used to calculate best value.