TABLE 7. Barium I–II transition at 25 °C

Researchers	Transition pressure (kbar)	Temp.	Method of detection
Bridgman (1942)	(e) 59	23 °C Room temp.	Volume
Bridgman (1952)	(c) 78	Room temp.	Electrical resistance
LaMori (1963)	(e) 59.1	25 °C	Electrical resistance
Jeffery, et al. (1966)	(e) 53.3	25 °C	X-ray diffraction and electrical resistance
Jeffery, revised (1968)[a]	(e) 54.7[b]	25 °C	
Vereshchagin, et al. (1966)	(c) 58.5		
Haygarth, Getting and Kennedy (1967)	(e) 54.7[b] (e) 55.0	22 °C	Electrical resistance
Zeto and Vanfleet (1969)	(e) 56.273[b]	25 °C	Electrical resistance
Best Value	55.3 ± 1.2	25 °C	

(e) equilibrium; (c) compression; (s) shock.

[a] Based on NaCl compression data of Jeffery, et al. (1966); pressure obtained from Decker's (1968) revised equation of state for NaCl (Decker, 1971).

[b] Best value an average of these three values.

studies at pressures from 88 kbar to 129 kbar. In the early nineteen sixties more serious attempts were made to determine this transition pressure.

As a result of a series of measurements, Balchan and Drickamer (1961) reported the Bi III–V transition at 89–92 kbar and used the value of 90 kbar as the accepted value. Using the pressure scale of Kennedy and LaMori (1962), Klement, Jayaraman, and Kennedy (1963) determined the phase diagram of bismuth up to 70 kbar and 460 °C. Four points were located by DTA methods on the Bi III–V boundary. From linear extrapolation through these four experimental points, a pressure of 82 kbar at 25 °C was estimated, but allowing for curvature in the phase boundary such as was indicated, the authors estimated a transition pressure of 78–82 kbar at 25 °C. Giardini and Samara (1965) re-examined the upper bismuth point using a "manganin gage with multiple-event resistance cell". Using an extrapolation based on the value of 59 kbar for the fixed point of barium, they concluded that the upper limit for the Bi III–V transition was no higher than 81–82 kbar. These measurements all refer to the initiation of a resistance transition on the increasing pressure cycle.

Stark and Jura (1964) used a unique method in an attempt to approach thermodynamic equilibrium for several high-pressure transitions. Due to the fact that the transition pressure observed under compression is always higher than the thermodynamic equilibrium transition pressure, a method of heating the sample by an electrical pulse of millisecond duration was employed to thermally activate the transition. In order for this method to work, dP/dT must be negative. When an electrical pulse is sent through the sample, it is heated high enough to transform some of the material to the higher pressure phase. When the pressure is not in the region of a phase boundary, the resistance returns to its initial value in a time less than a minute. The transition point is determined when the resistance returns to its value in the high-pressure phase. It is important that the material studied have no thermally activated metastable state. The Bi III–V transition was reported at 82 ± 4 kbar by this method while a value of 88 kbar was reported with conventional measurement on the compression cycle.

With the use of x-ray diffraction and Decker's (1966, 1971) NaCl pressure scale, Jeffery, et al. were able to isolate the nucleation hysteresis and report an equilibrium transition pressure of 73.8 kbar for the Bi III–V point. The equilibrium value was taken as the midpoint of the nucleation hysteresis interval. Later, improved measurements of the zero-pressure compressibility data used in Decker's semi-empirical equation of state revised the transition pressure value to 76.0 ± 1.3 kbar. (See section 4 of this review.)

Vereshchagin, et al. (1966) published a value of 89.2 kbar ± 1 percent and stated that the measurement was made in a free-piston gage. Since little description of the technique and virtually no experimental details were given, no meaningful evaluation of this work can be made. Haygarth, et al. (1969) reported a value of 77.5 ± 1.0 kbar for Bi III–V equilibrium transition pressure. This value was based on a short extrapolation of the Bi III–V phase line as measured in the piston-cylinder system used for the Ba I–II calibration and one unrepeated direct measurement of the transition point at 25 °C. Equilibrium was taken as the average of increasing and decreasing cycle in which both apparatus and sample hysteresis were present.

The work of Jeffery, et al. (1966) and Haygarth, et al.

represent the only two studies which are not dependent on an extension of an apparatus calibration referred to the Ba I–II transition. These other studies used a value of 59 kbar for the Ba I–II transition from Bridgman's volume work, and the lowering of this value as discussed above naturally will reduce the reported values for the Bi III–V transition. Jeffery, et al. have better means of eliminating apparatus hysteresis and thus determining the true sample hysteresis, but the use of a theoretical equation of state leads to uncertainty. The method of Haygarth, et al., is more direct, but uncertainties associated with hysteresis effects and extrapolation are more serious. As in their work on barium, Haygarth, et al. report only reproducibility flags and not absolute accuracy error flags. For these reasons the reviewers conclude that only the results of the two studies mentioned be used in the evaluation of a "best value" and that an error of 1.8 kbar be used for each of the studies. This approach equally weights the two studies and yields a value of 76.7 ±1.8 kbar for the Bi III–V transition.

3.5. Fixed Points Above 80 Kbar

Just as the calibration studies of the Hg L–α and the Bi I–II transformation points differ in nature from the calibration studies in the 30–80 kbar range, the calibration of points above 80 kbar differs from the studies below 80 kbar. Historically, calibration of points has been based upon extrapolated load vs pressure curves and on comparisons with shock data, both of which are much less reliable than the methods previously discussed.

Several reference points have been identified, and values have been established for the increasing pressure cycle. The severity of the hysteresis in transitions in this pressure region has not been studied systematically.

a. Tin

Stager, Balchan, and Drickamer (1962) were the first to detect and measure the Sn I–II transition, and they published a value of 113–115 kbar on the basis of thirteen determinations.

Barnett, et al. (1966) reported the value 92 ±3 kbar for the initiation of this transition on the compression cycle. On the basis of Decker's (1971) equation of state for NaCl, a new value of 94.0 ±3 kbar is calculated. Since measurements were taken only on the compression cycle, no value for the equilibrium transition pressure of tin was calculated.

Stark and Jura (1964) obtained a transition pressure of 99 ±4 kbar using their method of thermal shock.

b. Iron

The pressure-induced phase transition in iron was discovered by means of shock-wave techniques and was reported to occur at 130 kbar (Bancroft, et al., 1956; see table 10). When corrected to the hydrostat, the pressure would be about 128 kbar. Bancroft, et al. also observed some effect of sample thickness, indicating that the shock times are possibly shorter than or of the same order of magnitude as the transition time. Later shock measurements (Loree, et al., 1966) gave 127 ±1 kbar after the strength-of-material correction. These measurements are probably not reliable for calibration of static systems as discussed in section 5.

The iron phase transition has also been studied by static techniques (Balchan and Drickamer, 1961; Takahashi and Bassett, 1964; Clendenen and Drickamer, 1964; Bundy, 1965; Mao, et al., 1967; Millet, 1968; Takahashi, et al., 1968; Stark and Jura, 1964; Takahashi, unpublished). Pressure measurements resulting from the shock and static work are reviewed in table 10.

The principal disadvantage of iron as a fixed point on

TABLE 8. Bismuth III–V transition at 25 °C

Researcher	Transition pressure (kbar)	Error (kbar)	Method of detection
Bridgman (1952)	(e) 88		Volume
Bundy (1958)	(c) 122		Electrical resistance
Balchan and Drickamer (1961)	(c) 89–92		Electrical resistance
Klement, Jayaraman, and Kennedy (1963)	(x) 78–82		
Stark and Jura (1964)	(e) 82	4	Electrical resistance
Giardini and Samara (1965)	(c) 82		Inductive coil
Jeffery, Barnett, Vanfleet, and Hall (1966)	(e) 73.8	1.3	X-ray diffraction electrical resistance
Jeffery, revised (1968)[b]	(e) 76.0 [a]	1.8	
Vereshchagin, et al. (1966)	(c) 89.3	0.9	
Haygarth, Ludemann, Getting, and Kennedy (1969)	(e) 77.5 [a]	1.0	Electrical resistance
	78.2	1.0	
Best Value	76.7	1.8	

(e) equilibrium; (c) compression; (s) shock; (x) extrapolation of phase diagram.

[a] Values used to determine best value.

[b] Pressure obtained from Decker's (1968) revised equation of state for NaCl (Decker, 1971).