ual drift should be long-term low-temperature strain annealing. Similar precautions must be taken in pressure gages, but the allowable size places a serious restriction in this regard. It is significant to realize that a drift in the zero-pressure resistance of a coil does not necessarily imply a loss of calibration of the coil since the pressure coefficient indicates only the percentage change. Conversely, it is possible, but not as logical, that a change in pressure coefficient could occur without a zero drift occurring. Johnson (1963) reported a change of one ppm/week in the zero resistance value, but less than one bar effective difference in eight kbar over a period of 100 days.

Although earlier work (Bridgman, 1911a) implied manganin coils exhibit good long-term stability, later work with improved sensitivity demonstrated the limitations of these coils. Bridgman (1940a, b) reported changes in the pressure coefficients of a few parts in 10^3 over a period of two months, and Adams, Goranson, and Gibson (1937) reported constant coefficients "to one part in 10^3" for several months. Boren, Babb, and Scott (1965) reported a drift of the zero-pressure resistance of slightly less than one part in 10^4 for a well-seasoned coil in two months. Definitive work has not been reported and appropriate effort has not been made to determine and improve the long-term stability of manganin gages when changes in the ppm range are considered.

d. Variation of Resistance and Pressure Coefficient with Temperature

The variation of the resistance with temperature for a typical sample of manganin is shown in figure 2. Since manufacturers generally will guarantee only a room temperature coefficient of less than 20×10^{-6} $°C^{-1}$, a temperature control of at least 0.1 °C must be used for high-pressure work to be reproducible to at least one bar if one assumes that the shape and position of the resistance vs. temperature curve is not dependent upon pressure. It is desirable to have the maximum of the resistance curve at room temperature or the operating temperature of the gage. Commercially available manganin is manufactured with this principle in mind. Adams, Goranson, and Gibson (1937) have indicated, however, that a seasoning treatment of 140 °C for ten hours increased the maximum by approximately 10 °C. Johnson (1963) has reported an increase of 10 °C in the position of the maximum with an applied pressure of eight kbar, and Wang (1967) has reported a shift of approximately 3 °C at four kbar with little change in shape of the curve. Assuming that the shift is linear with pressure and that the shape of the curve does not change, a gage operating at 50 kbar and room temperature would be operating 40 °C–60 °C from the maximum, which would result in a temperature coefficient of approximately 50×10^{-6} $°C^{-1}$ at 50 kbar. This result suggests temperature control of approximately 0.02 °C is necessary to maintain repeatability of one bar. This simple approximation illustrates the need for a

material with a lower temperature coefficient than manganin over a larger temperature and pressure range.

If a coil is calibrated at a given controlled temperature and used only at that temperature, the complete pressure and temperature dependence of the resistance is not required, only the pressure variation. In practice, however, the complete function would be desirable. As indicated by Wang (1967); by Adams, Goranson, and Gibson (1937); by Michels and Lenssen (1934); and by Bridgman (1940a, b) the pressure coefficient is almost independent of temperature below 10 kbar. These workers report changes of 0.01 percent, 0.013 percent, 0.013 percent, and 0.022 percent in the pressure coefficient for a one-degree change in temperature, and each indicates that their value is only approximate. These quantities are so small they require resistance measurements in ppm to observe. Since the manganin gage is currently being used to pressures of 50 kbar (Barnett and Bosco, 1967), further work on the complete functional relationship of resistance with pressure and temperature at higher pressures is needed.

e. Linearity of the Resistance Change

There is, of course, no fundamental reason that the resistance change in manganin is linear with pressure. Bridgman and Lisell simply observed this fortuitous result to be true within the accuracy of their original measurements. As primary gages were improved and extended to pressure above a few kilobars the extent of nonlinearity became apparent. Bridgman (1940a, b) reported a discrepancy of approximately two percent in pressure between a linear extrapolated calibration and a primary measurement at 25 kbar and introduced a calibration curve in which pressure is expressed as a second-order variation with change of resistance:

$$P = A\Delta R + B(\Delta R)^2. \tag{33}$$

Bridgman determined the constants A and B using the mercury freezing point at 0 °C and the Bi I–II room-temperature solid-solid transition. Such a two-point calibration technique is now generally considered necessary if accuracies better than one or two percent in pressure are desired, especially above ten kbar. Even below ten kbar Babb (1963) has shown the need for a two-point calibration and has discussed variations from the previous linear calibrations used by Bridgman. The best study of linearity is that of Boren, Babb, and Scott (1965), who used five fixed points (H_2O I–III–L, Hg L–I at −25 °C, Hg L–I at +20 °C, and Bi I–II with nominal pressures of 2090, 2525, 7450, 11500, and 25100 bar respectively) to overdetermine the two coefficients A and B. They found a fit which agreed at all five points to within three bars. These data indicate that there is no need for a third-order term in the calibration expression until greater accuracy is obtained in the fixed-point calibration pressures. At 25 kbar the second term in the ex-

pression contributes approximately 0.8 kbar, approximately three percent, to the pressure value for the particular coil. If a single-point calibration were made using the mercury-0 °C calibration point, the calibrated pressure would have deviated from the accepted pressure by only two percent. The authors report uncertainties on the coefficient A in equation (33) of 0.035 percent and on B of 1.2 percent based on statistical analysis of a least-square fitting to a given set of five calibration values. If one includes the variation due to the uncertainty of the reported calibration pressures, the values of A and B are less well-defined. The B coefficient is highly dependent upon the value used for the Bi I-II point since it is rather far removed from the other points. The coefficient B is uncertain to approximately ten percent as a consequence of the 60 bar uncertainties in the Bi point reported by Heydemann (1967).

Since a manganin gage has recently been used to 60 kbar in a hydrostatic environment by Barnett and Bosco (1967), the curvature and shape of the calibration curve above 25 kbar is now becoming of interest. Zeto and Vanfleet (1969) have made calibration intercomparisons between manganin and the fixed transition pressures, Hg I-L (20 °C), Bi I-II Tl I-II and Ba I-II at nominal pressures of 11 kbar, 25 kbar, 37 kbar, and 55 kbar respectively. The main thesis of these authors was an argument that the Ba I-II transition was significantly lower than the previously accepted pressure of 59 kbar. Since their paper was published, a lower value for the barium transition has been widely accepted (see section 3 of this review). It is thus now possible to use their data to evaluate the behavior of a manganin gage at pressures to 60 kbar based upon the independently determined transition pressure of Ba.

As discussed in section 3 of this review, the Hg I-L, Bi I-II, and the Ba I-II transitions appear to be the best-known calibration pressures in their respective pressure regions. Taking values of $\Delta R/R$ from the work of Zeto and Vanfleet with pressures from Zhokhovskii (1957), Heydemann (1967a), and Haygarth, et al. (1967), as shown in table 17 a one-point, a two-point, and a three-point calibration can be made and yields the equations for the pressure in kbar:

$$P_1 = 426.82 \left(\frac{\Delta R}{R} \right)$$

<div align="right">using Hg I-L only   (34)</div>

$$P_2 = 417.61 \left(\frac{\Delta R}{R} \right) + 338.2 \left(\frac{\Delta R}{R} \right)^2$$

<div align="right">using Hg I-L, and Bi I-II only   (35)</div>

$$P_3 = 412.61 \left(\frac{\Delta R}{R} \right) + 606.9 \left(\frac{\Delta R}{R} \right)^2 - 3131 \left(\frac{\Delta R}{R} \right)^3$$

<div align="right">using Hg I-L, Bi I-II and Ba I-II.   (36)</div>

TABLE 17. Fixed point vs manganin gage intercomparison values

Transition	Pressure (kbar)	$\frac{\Delta R}{R} \times 100$	Temperature
Hg I-L	11.627	2.7241	20.36°
Bi I-II	25.608	5.8545	23.5°
Tl I-II	36.564	8.2806	23.5°
Ba I-II	54.7	12.3317	22.0°

Figure 5 illustrates the differences of $(P_2 - P_1)$, $(P_2 - P_3)$, and $(P_3 - P_1)$ for comparison as they vary with a nominal pressure P_3. If the Tl I-II transition with manganin data from Zeto and Vanfleet is used, a third-order least square fit yields coefficients in equation 36 only slightly different from those given which implies the Tl I-II value used is consistent with the Bi I-II value of Heydemann. The rather strong third-order term and divergence from the second-order equation suggests either (1) the above third-order equation is not a good form of the resistance-pressure relationship, (2) the pressure calibration values used are still not reliable, or (3) the data of Zeto and Vanfleet are in serious error. At this writing it appears that the first of these alternatives is the most probable. The precise calibration of the manganin gage in the region between 25 and 50 kbar will require extensive work due to unknown nonlinear terms. This nonlinearity may well be associated with a change
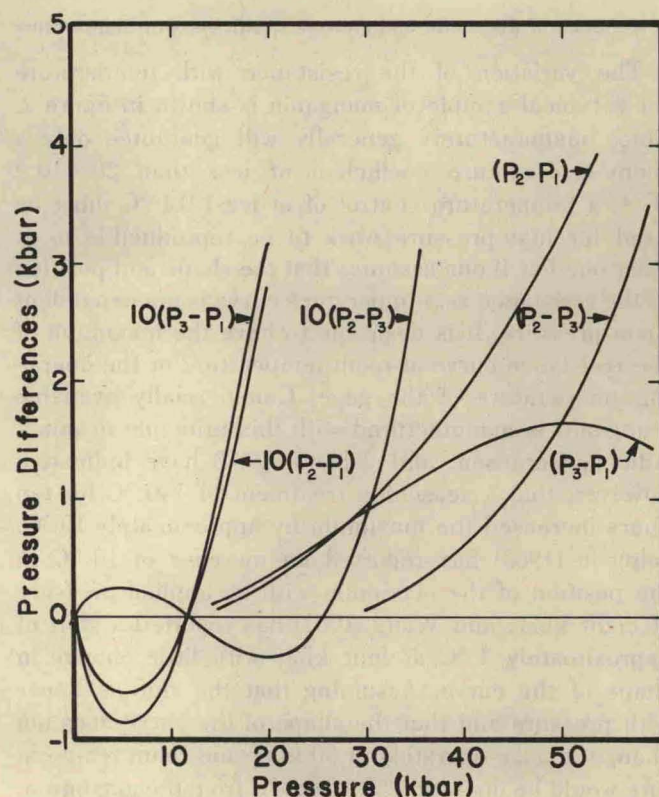

FIGURE 5. Variation between a linear (P_1), quadratic (P_2) and cubic (P_3) calibration curve for a manganin gage using Hg I-L; Hg I-L with Bi I-II; and Hg I-L, Bi I-II and Ba I-II respectively.