

the wire suddenly increased by a factor of about 2.2. Thus the melting temperature was sharply defined at each pressure.

Because the wire was tightly confined at these pressures it was possible to melt the wire successively many times, changing the pressure after each melting. The ram loading was calibrated to indicate pressure by measuring the resistance transitions in Bi (25.4 kbar), Tl (37 kbar), and Ba (58 kbar), and interpolating between these values with a smooth curve.

### III. MELTING CURVE

The temperature of melting was taken as the temperature at the beginning of the sudden resistance rise as indicated in Fig. 2. Because of the sharpness of the break in the resistance curve one can determine this point to better than  $\pm 2^\circ\text{C}$ . The accuracy of any temperature measurement however is probably only about  $\pm 10^\circ\text{C}$ , even though the thermocouple calibration at atmospheric pressure was accurate to  $\pm 5^\circ\text{C}$  at these temperatures, because no pressure correction to the thermal emf was attempted.<sup>23</sup>

Each run consisted of a set of melting points at various pressures. The results of the four successful melting runs did not all lie on the same curve. This could be due to variation in the thermocouple calibration or to thermal gradients along with the difficulty of placing the thermocouple junction at a point corresponding to the hottest region along the gold wire. Temperature gradients, large enough to account for the differences, are evident from the width of the transition which was between 20 and  $30^\circ\text{C}$ . In order to correct for this uncertainty the temperatures of each run were all raised or lowered by an amount such that the melting curves extrapolated to the correct melting point at atmospheric pressure with the slope calculated from Clapeyron's equation.<sup>24</sup> The corrections amounted to  $-13$ ,  $-11$ ,  $+5$ , and  $+11^\circ\text{C}$  for the four runs. After this correction all points from all runs lay on a single smooth curve with a maximum scatter less than  $\pm 7^\circ\text{C}$ .

Another correction should be applied to the raw data because the pressure calibration was at room temperature rather than at the temperature of the experiment. The pressure cell expands with increasing temperature causing the pressure to rise. This does not appear as an increase on the oil pressure behind the rams because of internal friction in the pyrophyllite and friction in the pistons themselves. Above 40 kbar the gaskets are essentially immovable and it was assumed that the pressure increase due to heating was proportional to the temperature change from room tempera-

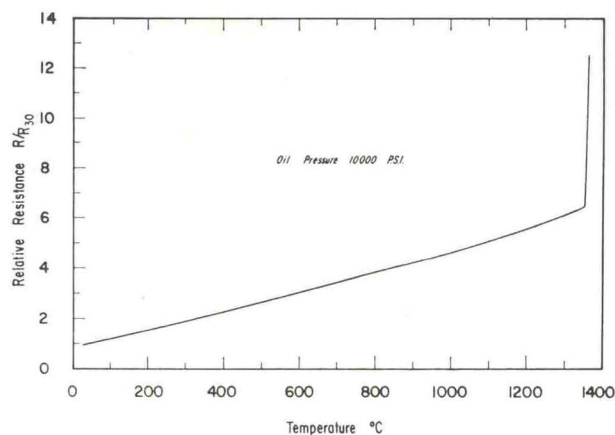


Fig. 2. Relative resistance of gold as a function of temperature at 10 000-psi oil pressure. (10 000-psi oil pressure corresponds to 52.2 kbar for the sample at room temperature.)

ture to the melting point. Below 15 kbar the gaskets are still forming and as the volume expands more material is forced into these gaskets between the anvils giving no pressure increase in this range. Between 15 and 40 kbar the correction was assumed to vary smoothly from 0 to the value at 40 kbar. Evidences for the above assumptions are: (a) Upon cooling the sample after melting at a pressure less than 15 kbar one notes a drop in the oil pressure. This indicates that the volume after the heating cycle is less than before allowing the rams to move in and the oil pressure to drop. (b) The raw melting curve between 15 and 40 kbar shows a slight upward curvature which is removed by applying the proposed pressure correction. The amount of the pressure correction above 40 kbar is not known so it was determined from the melting curve itself by assuming that this curve should have the form of Simon's equation.

The method of obtaining the pressure correction along with the coefficient  $c$  in Eq. (9) is outlined below. Substitution of  $T_m = T_{m,0} + \delta T$  into Eq. (9) and expanding in a power series in  $\delta T/T_{m,0}$  yields the following equation after some manipulation:

$$P_m - P_0' \delta T = \frac{(c-1)P_0'}{2} \frac{(\delta T)^2}{T_{m,0}} \left[ 1 + \frac{c-2}{3} \frac{\delta T}{T_{m,0}} \dots \right]. \quad (10)$$

If one plots experimentally measured values of  $(P_m - P_0' \delta T)$  versus  $(\delta T)^2$  as in Fig. 3 the points indicated by the open circles are obtained. The desired pressure correction is applied to the measurements above 40 kbar so as to cause them to fall along a curve satisfying (10) with a least-mean-square deviation. The final results are represented by the closed circles with  $c = 2.2 \pm 0.1$  and a maximum pressure correction of 3.9 kbar at 66.7 kbar. The corrected results are finally graphed in Fig. 4.

<sup>23</sup> F. P. Bundy, J. Appl. Phys. **32**, 483 (1961).

<sup>24</sup> It is to be noted that one set of measurements, shown by the point numbers 2, 3, 4, 5, 7, 8, and 10 in Fig. 4, extend down to 3.5 kbar and have an initial slope of  $5.9 \pm 0.2^\circ\text{C}/\text{kbar}$  in excellent agreement with the value  $5.91^\circ\text{C}/\text{kbar}$  calculated from Clapeyron's equation.



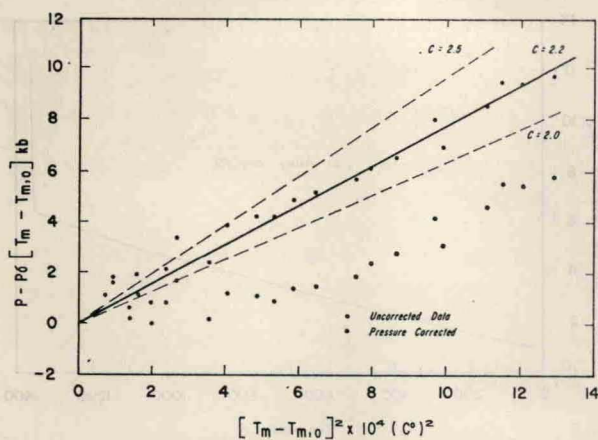


FIG. 3. Normalized melting pressure as a function of the square of the increase in melting temperature. This curve is used in the determination of the Simon equation parameter.

#### IV. RESISTANCE MEASUREMENT

The high-temperature measurements were made by heating the sample to the melting point at several fixed pressures. As discussed in the previous section the pressure increases as the temperature is raised. By using the pressure increase determined at the melting point and assuming a linear increase with temperature at intermediate points a small pressure correction was applied to the raw data. The results from 9 different samples are shown in Fig. 5 where the reference temperature  $T_0$  was taken at 30°C. One can never be sure that the application of pressure will not alter the dimensions of the specimen; thus all results are given relative to the resistance at room temperature at each pressure. The initial decrease in  $r_p(T, T_0)$  was calculated using Eq. (4) in which the compressibilities were estimated using Grüneisen's relation,  $K_T = \alpha V / \gamma C_v$ , with experimental values of thermal expansion.<sup>25</sup> The calculated decrease is shown as a solid line in Fig. 5. The data

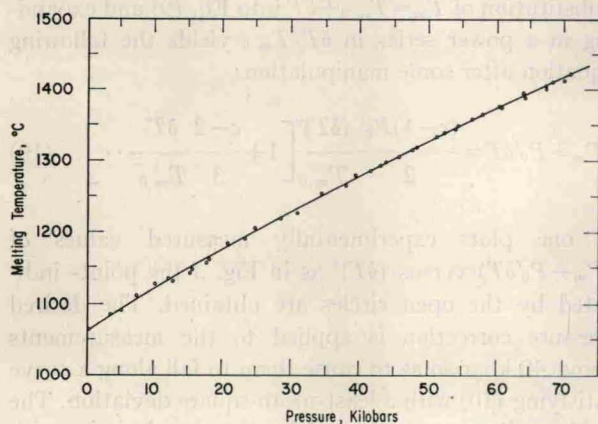


FIG. 4. Pressure dependence of the melting temperature of gold.

<sup>25</sup> See Refs. 8 and 9.

at higher temperatures appear to fall below this calculated curve. It is possible that the difference is due to the decrease in the equilibrium number of vacancies at high pressures.<sup>26</sup> The vacancy contribution to the resistance can be estimated from the measurements of Meechan and Eggleston.<sup>27</sup> The dashed curve in Fig. 5 is the calculated resistance ratio including the effect of vacancies.

The initial heating cycle generally gave a slightly larger value for  $r_p(T, T_0)$  than successive cycles even at the same pressure. This may cause the results to be too low at higher pressures. To check this possibility, four runs were made at about 53 kbar, each sample being melted only once, and the resistance measured only on

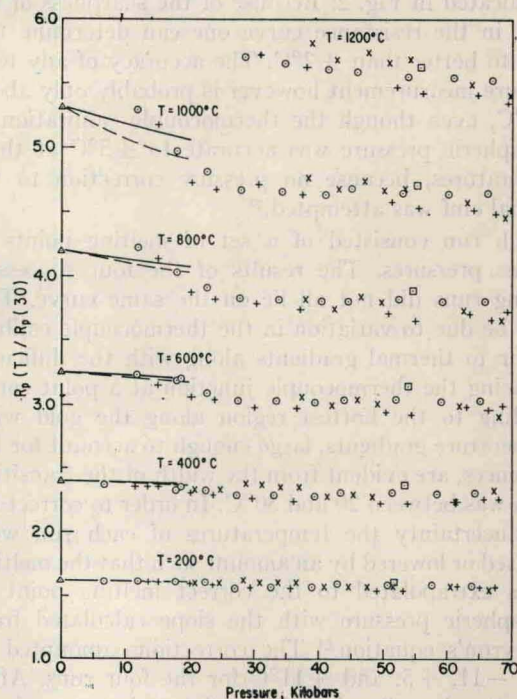


FIG. 5. Resistance of gold at temperature  $T$  to that at 30°C as a function of pressure. The solid line follows the calculated initial slope at zero pressure and the dashed line is the calculated curve after a vacancy correction is made.

the initial temperature increase. The average of these results, as shown by the squares in Fig. 5, was slightly higher than the other measurements but not significantly so. As the temperature increased the surrounding BN became conducting, the insulation resistance dropping to about 10  $\Omega$  at the melting point. This was due to a black substance that would form over the surface of the BN above 600°C. This material proved to be conducting and tended to short out the gold at high

<sup>26</sup> H. H. Grimes, National Aeronautics and Space Administration Technical Note, NASA TN D-2371, UR-64-201366 (National Aeronautics and Space Administration, Washington, D. C., July 1964).

<sup>27</sup> C. J. Meechan and R. R. Eggleston, *Acta Met.* 2, 680 (1954)