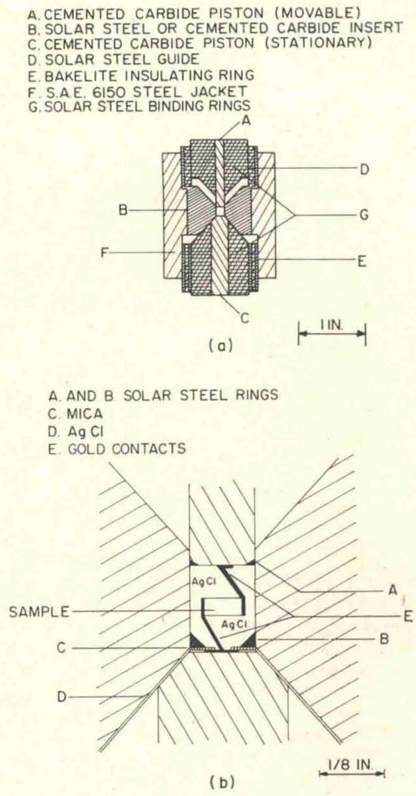

FIG. 3. (a) The piston-cylinder device which contains the high pressure at low temperatures. A thermocouple and a carbon resistor are located in holes drilled into part D. Four-lead resistance measurements are made between the top of piston A and the bottom of piston C. (b) A magnified view of the high-pressure sample chamber. All electrical contacts are pressure contacts. Electrical insulation is provided by mica C and AgCl D.

Sample pressure was monitored with a strain-gauge pressure cell in the hydraulic line of the ram shown in Fig. 2. The output voltage of the pressure cell was applied to the X axis of the X–Y recorder, thereby giving a continuous plot of resistance versus pressure which is invaluable in detecting transitions. No attempt was made to use extremely slow pressurization rates. Pressure was typically applied at a rate of about 1 kbar/min. Several runs were made with much slower pressurization rates but no appreciable difference was noted in the observed transition pressures.

The sample pressure must be deduced indirectly from the pressure in the hydraulic line. It cannot be calculated simply as applied force divided by piston area because of losses due to friction in the hydraulic ram, friction between the piston and cylinder in the high-pressure cell, and friction between the AgCl medium and the cell walls. The sample pressure is inherently nonhydrostatic because of the use of a solid pressure-transmitting medium and uniaxial loading. However, we may reasonably assume that the axial pressure gradients are much larger than the radial gradients and neglect the latter in what follows. Thus for the increasing pressure stroke we represent the pressure as being constant in horizontal strata parallel with the piston face and decreasing downward from a maximum just below the piston. The neglect of data obtained on the decreasing pressure stroke is reasonable due to the metastability of bismuth II and III as reported by Brandt and Ginzburg.[8] Also this has become common practice among high pressure investigators using solid pressure transmitters, e.g., Il'ina and Itskevich.[9]

By considering the balance of forces on a thin disk of the AgCl we obtain

$$(\pi D^2/4)\,dP=\pi DS\,dx, \tag{1}$$

where D is the i.d. of the high-pressure cell, and S is the shear strength of the AgCl. The expression on the left of Eq. (1) represents the downward force due to the pressure differential across the disk, and the expression on the right of Eq. (1) represents the upward resistance offered by the shearing of the AgCl at the cell wall. The disk being considered is located a distance x below the piston face.

According to Bridgman[12] the shear strength of AgCl increases approximately linearly with pressure. Thus

$$S=S_0+\alpha P, \tag{2}$$

where the material parameters S_0 and α are independent of pressure but vary with temperature. Inserting (2) into (1) and integrating yields

$$P(x)=[(P_A-P_F+S_0/\alpha)\exp(-4x\alpha/D)]-S_0/\alpha. \tag{3}$$

We have used the boundary condition that at the piston face, $x=0$, $P=P_A-P_F$. P_A is the applied pressure calculated from the hydraulic pressure neglecting all

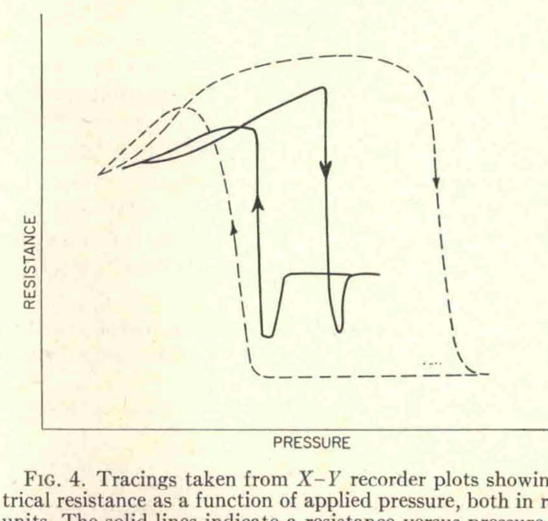

FIG. 4. Tracings taken from X–Y recorder plots showing electrical resistance as a function of applied pressure, both in relative units. The solid lines indicate a resistance versus pressure run at 249°K and the dashed line represents a run at 77°K. Note the difficulty of determining the beginning of the transition at 77°K. For this reason the pressure on the increasing stroke at half the discontinuity is used as the transition pressure.

losses, and P_F represents the losses due to friction in the hydraulic ram plus those due to friction between the piston and cylinder in the high-pressure cell.

The sample pressure was calculated from (3) by inserting the value of x appropriate to the sample position and the value of P_A observed at the midpoint of the phase transformation. The midpoint of the transition was taken to be that pressure at which the sample resistance had changed by one-half the discontinuity associated with that transition. This procedure avoided the difficulty of determining the beginning or end of the transition which became poorly defined at low temperatures (see Fig. 4).

In order to evaluate Eq. (3) we need to know the shear strength of AgCl as a function of temperature and pressure. Bridgman[12] measured the shear strength of AgCl up to 50 kbar at room temperature and Towle[13] measured the shear strength of AgCl down to 77°K at atmospheric pressure. By combining these data with the melting curve of Deaton[14] and the empirical shear strength equation of Towle[15] we were able to calculate the values of the parameters α and S_0 at all the temperatures required. Some representative values are given in Table I. Finally the frictional term, P_F, was determined by normalizing our room-temperature results on the bismuth I–II transition pressure to the value 25.5 kbar. This value for the bismuth I–II transition pressure at room temperature was agreed upon at the "Symposium on the Accurate Characterization of the High-Pressure Environment" held at the National Bureau of Standards in 1968. Within experimental error it also agrees with the result obtained by Heydemann[16] in his accurate measurements. The value of P_F thus determined was typically 2 kbar and was assumed to be independent of temperature.

IV. RESULTS

The resulting phase diagram is shown in Fig. 5. There is good agreement with extrapolations of the data of Tikhomirova *et al.*[7] and also with the two points determined by Bridgmen[1] at 223°K. There is also good agreement with Brandt and Ginzburg's[7] result at 77°K. Ignoring for the moment the question of a new phase of bismuth we find fair agreement between our phase diagram and Il'ina and Itskevich's.[9] There is

TABLE I. Representative values for the material parameters S_0 and α [see Eq. (2)] used in determining the sample pressure are given for several temperatures.

T(°K)	S_0 (bar)	α
300	300	0.0205
200	520	0.0273
100	870	0.036
4.2	1520	0.0473

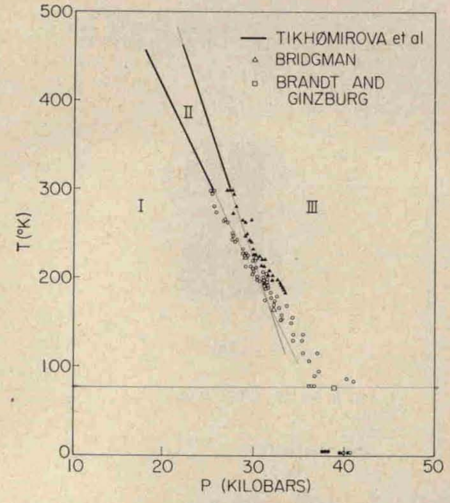

FIG. 5. The phase diagram of bismuth below room temperature as determined by the present author. The open circles represent the bismuth I–II or I–III phase boundaries. The closed triangles belong to the bismuth II–III phase boundary; however, the data points below about 225°K should not be used as an indication of the actual phase boundary because of the large uncertainty discussed in the text. The closed circles at 4.2°K represent one run in which the hysteresis loop was exceptionally small due to extrusion of some of the AgCl pressure-transmitting medium as described in the text. The open triangles refer to Bridgman's data (Ref. 1). The solid lines are straight lines drawn through the data of Tikhomirova *et al.* (Ref. 6). The open square is a point determined by Brandt and Ginzburg (Ref. 7).

some disagreement regarding the II–III phase line and the I–III phase line. This could be due to the fact that we assume corrections to transition pressures due to AgCl pressure-transmitting medium are much greater than the corrections associated with the metastability of bismuth II and III as reported by Brandt and Ginzburg[8] and also Il'ina and Itskevich.[9] Corrections due to metastability would certainly lower our transition pressures, especially at low temperatures. This could improve agreement between our results and those of Il'ina and Itskevich, but considering the scatter in our data, the agreement would still be questionable. In any case the agreement observed between our results and those cited above indicates that our method of determining the sample pressure is satisfactory. This is reassuring considering that the hysteresis loops associated with pressure cycling were about 8 kbar at 300°K, 22 kbar at 77°K, and 40 kbar at 4.2°K. One notable exception occurred during one run at 4.2°K. A loud crack was heard accompanied by a large change in sample resistance. Subsequent pressure cycling at 4.2°K produced a pressure hysteresis loop width of only 15 kbar for the phase transition. Later examination revealed that a large amount of AgCl had extruded up out of the cell, but that the sample and electrical leads had remained intact. The extrusion greatly reduced the length of the AgCl column which had previously caused a frictional loss along the wall of the cylinder and hence, greatly reduced the width of