$$(S_A)_l=-\frac{\partial \mu_A^\circ}{\partial T}, \qquad (S_B)_l=-\frac{\partial \mu_B^\circ}{\partial T}$$

and

$$(\Delta S)_l=(S_A)_l-(S_B)_l.$$

Since the entropy change during melting is

$$\Delta S_m=S_l-S_S=(S_A)_l-x\,(\Delta S)_l-S_S-R\{(1-x)\ln(1-x)+x\ln x\},$$

the difference of ΔS_m along the melting curve is

$$d\,(\Delta S_m)=d\,(S_A)_l-dS_S-x\,d\,(\Delta S)_l-(\Delta S)_l\,dx-R\{-\ln(1-x)+\ln x\}dx. \tag{10}$$

Here it should be noted that $(S_A)_l$, $(\Delta S)_l$ and S_S are the values which depend on a species or a solid phase, that is, their variations depend predominantly on the variations of the thermal entropies. In general they are small and may be negligible compared with the variation of x. Therefore eq.(10) becomes

$$d(\Delta S_m)=-\left\{(\Delta S)_l+R\ln\frac{x}{1-x}\right\}dx, \tag{11}$$

and ΔS_m has the maximum under the condition

$$\ln\frac{x}{1-x}=-\frac{(\Delta S)_l}{R}. \tag{12}$$

Following Rapoport $(\Delta S)_l$'s for cesium and tellurium are −1.0 cal/deg.mole and 0.154 cal/deg·mole respectively[8]. Substituting these values into eq.(11), the compositions xs, corresponding to the maxima of the entropy changes during melting, are determined. And we can derive the pressures, at which entropy changes of melting show the maxima, as about 30 Kb for cesium and about 5 Kb for tellurium respectively.

These values may be verified by the observations of the latent heats of fusion under high pressure. However the experiments are not easy.

Pressure and Temperature Dependences of the Electrical Resistance of Bismuth

The transition curves of bismuth have been confirmed by many investigators and the correct phase diagram has been obtained. It is shown on Fig. 3[14]. However the crystal structures of high pressure phases are not yet determined. The bismuth I lattice can be described in two ways, as a lattice in which the rhombohedral angle is nearly 90°, the unit cell containing eight atoms, or as a rhomboheral lattice with an angle α which is nearly 60°, the unit cell containing two atoms. The atoms are arranged in double layers, each atom having three near neighbors in the double layer in which it is situated, and three others at a greater distance in an adjacent layer[15]. The bismuth II lattice is presumed as a body center cubic like structure[16] or a hexagonal structure[17]. The higher pressure phases are not yet known.

On the other hand in liquid bismuth at atmospheric pressure there are about eight nearneighbors[18]. The volume change during melting is negative in bismuth I region.

The electric resistance of the liquid bismuth up to 12 kb has been observed in detail by Bridgman[19], but the values at higher pressure had not been observed.

We observed them up to 280°C and 30 kb. The electric resistance of the liquid bismuth showed the characteristic change in the pressure range from

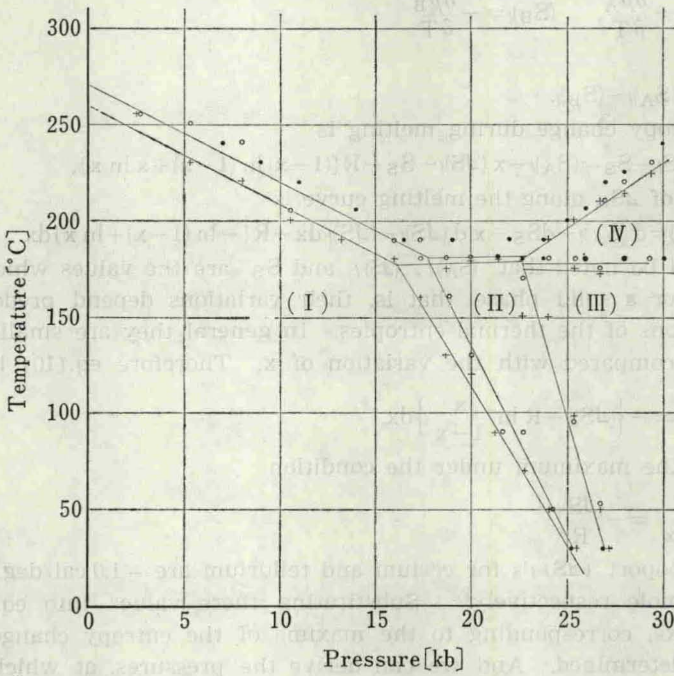

Fig. 3. The phase diagram of bismuth: observed by Jayaraman et al. ·; observed in typical 2 runs in our experiments —, 0, +.

15 kb to 25 kb.

High pressure was induced by the usual piston-cylinder devices. A sample bismuth was heated by a cyrindrical graphite tube set in talc, a pressure transmitting medium. Temperature was measured by the thermocouple of chromel-alumel, but the pressure effect on its thermoelectric force was neglected. The sample bismuth (prepared by Mitsubishi Kinzoku Kogyo Co., Ltd.) had a purity of 99.999% and the impurities were Au, Ag, Cu, Pb, Fe, Sb and As.

Fig. 4 shows the whole sample assembly and Fig. 5(a), 5(b) and 5(c) show the detailed arrangement of the sample holder. The hole, into which the bismuth was inserted, was drilled by the drill of 0.3 mm diam.. The bismuth was made as follows. A grain of the bismuth is put in a glass tube, the glass tube is heated until it becomes soft and then drawn in opposite directions in such a manner as the molten bismuth is drawn simultaneously. We can get a bismuth wire of an desired diameter in this manner. We neglect the chemical reaction during this process. The silver chloride chip under the sample holder was set to protect the transformation of the sample holder. The pyrophyllite chip on the sample holder was set to protect the sample holder from thrust of the alumina tube. The iron wires of 0.3 mm diam. on the market were used as the leads.

It is ideal that the measurements of electrical resistances are made by the potentiometer method, but its application seems to be very difficult under high