



Fig. 7. Calibrated pressure

experiment, the melting curve of bismuth was used. We shall explain the method using Fig. 7.

There are curves of four types in this figure, — shows the calibration curve at room temperature, — shows the ideal curve with no frictions, — shows the calibration curve at high temperature which includes the effects of heat on frictions in compression run and — shows the calibration curve at high temperature which we want.  $\Delta f_1$ ,  $\Delta f_2$ ,  $\Delta f_1'$ ,  $\Delta f_2'$  and  $\Delta f$  are the distances as represented in Fig. 7.  $P_0$  is a certain fixed point. We used the transition pressures of bismuth as  $P_0$ 's (Note the linearity of curves in this region). The third curve can be obtained as follows. At a given melting temperature, the melting of bismuth in the sample cell must occur at the same internal pressure in both compression run and decompression run. Therefore, if we increase the internal pressure along the calibration curve at room temperature noting melting points, and then, decrease pressure noting melting points, the calibrated decompression curve is obtained, and then,  $\Delta f$  is obtained. But this curve includes the decreases of the frictions in the two runs. The fourth curve is obtained by dividing these decreases into the part of the compression run and that of the decompression run. The assumption that the effects of heat on the frictions are equal in both compression run and decompression run means

$$\Delta f_1' = (1 - \alpha) \Delta f_1 \tag{1}$$

and

$$\Delta f_2' = (1 - \alpha) \Delta f_2. \tag{2}$$

The sum of the decreases of  $\Delta f_1$  and  $\Delta f_2$  must be equal to the decrease of frictions included in the decompression curve of the third curve, that is,

$$\Delta f = (\Delta f_1 - \Delta f_1') + (\Delta f_2 - \Delta f_2'). \tag{3}$$

Substituting eq.'s (1) and (2) into eq. (3), we have

$$\alpha = \frac{\Delta f}{\Delta f_1 + \Delta f_2}$$

and

$$\begin{aligned} \Delta f_1' &= \left( 1 - \frac{\Delta f}{\Delta f_1 + \Delta f_2} \right) \Delta f_1 \\ \Delta f_2' &= \left( 1 - \frac{\Delta f}{\Delta f_1 + \Delta f_2} \right) \Delta f_2. \end{aligned} \quad (4)$$

The frictions at pressure  $P_0$  in the compression run may be proportional to  $\Delta f_1$ , and that in the decompression run may be proportional to  $\Delta f_2$ , at room temperature. Moreover  $\Delta f_1$ ,  $\Delta f_2$  and  $\Delta f$  are the experimental values. Therefore, we can calculate the values of  $\Delta f_1'$  and  $\Delta f_2'$ , and we can obtain the calibration curve at high temperature. Fig. 4 shows the calibration curve obtained by this method.

The pressure distribution in vertical direction is complicated and variations have maximum at the center of the assembly in both compression run and decompression run. In addition, they are the inflection points (See Fig.'s 5 and 6).

## References

- 1) G. C. Kennedy and P. N. LaMori, "Progress in very High Pressure Research", p.304, Wiley, New York, (1961).
- 2) One of the fellows in our laboratory.
- 3) D. L. Decker, J. Appl. Phys., 36, 157 (1965).

## 2. Variations of Ionic Radii in Alkali Halides Under High Pressure

### Ions in NaCl Structure

At atmospheric pressure, to a fair approximation, ionic radii are additive quantities. In this chapter, it will be examined whether this approximation is also fair at high pressure or not.

The following modified Born-Mayer<sup>1)</sup> equation for the lattice energy of an ionic crystal is used in calculating the P-K relation.  $K$  is defined by  $k=V/V_0$ ,  $V$  is the volume of an ionic crystal under pressure  $P$  and  $V_0$  is the volume of the crystal under zero pressure. The reason why we don't start with experimental values of variations of volumes of ionic crystals under high pressure but theoretical values, will be understood later. The lattice energy  $E_L$  is given by

$$E_L = -\alpha \frac{e^2}{a} + Mb \exp\left(-\frac{a}{\rho}\right) \quad (1)$$

where,  $\alpha$ ,  $e$ ,  $a$ , and  $M$ , are the Madelung constant, the electric charge of an electron, the nearest neighbor distance and the coordination number.  $b$ ,  $p$  are the experimental parameters. Using the equilibrium condition  $dE_L/da=0$  and notation  $a_0$  as the nearest neighbor distance at zero pressure and absolute zero, we have

$$E_L = -\alpha \frac{e^2}{a} + \frac{\alpha e^2 \rho}{a^2} \exp\left(-\frac{a_0 - a}{\rho}\right). \quad (2)$$

If we consider the thermal term at finite temperature, the internal energy is written in the form

$$E = E_L + E_K,$$