

responds to the melting. Since a fairly high rate of temperature change was used for the measurement ( $\sim 20^\circ\text{C min}^{-1}$ ), a thermal hysteresis of about  $15^\circ\text{C}$  is apparently seen for the melting point. We determined the equilibrium melting point as the average of the two signals in cooling and heating processes. The melting point monotonically increases with increasing pressure as shown in Figs. 8 and 9. The DTA signal splits into two peaks above about  $4 \times 10^3 \text{ kg cm}^{-2}$ . This suggests that there is a new high pressure phase between the two DTA signal peaks. The phase is denoted as Phase VI in the present paper.

#### §4. Discussion and Conclusion

The resultant pressure-temperature phase diagram of  $\text{NH}_4\text{HSO}_4$  is shown in Fig. 8. Data obtained in the present work are indicated by open circles and short bars. The short bars indicate the pressure or thermal hysteresis observed for first order transitions. In the

figure the transition points reported by Bridgman<sup>2)</sup> and Polandov *et al.*<sup>3)</sup> are indicated by the closed figures. The present results are fully consistent with those of Bridgman and Polandov *et al.* It should be noted that the points given by Bridgman are representing the equilibrium ones. On the other hand, the experimental points of the II-III transition by Polandov *et al.* are not the equilibrium ones but data for only cooling process. Bridgman already reported a marked volume change accompanying the I-IV transition and stated that the pressure hysteresis of the transition becomes very large as temperature decreases. Polandov *et al.*<sup>3)</sup> also pointed out that the thermal hysteresis of the II-III transition gets progressively large as pressure increases. In general, a thermal hysteresis of a first order transition increases as the transition temperature decreases with varying pressure. The thermal hysteresis of the II-III transition in  $\text{NH}_4\text{HSO}_4$ , however, decreases as the transi-

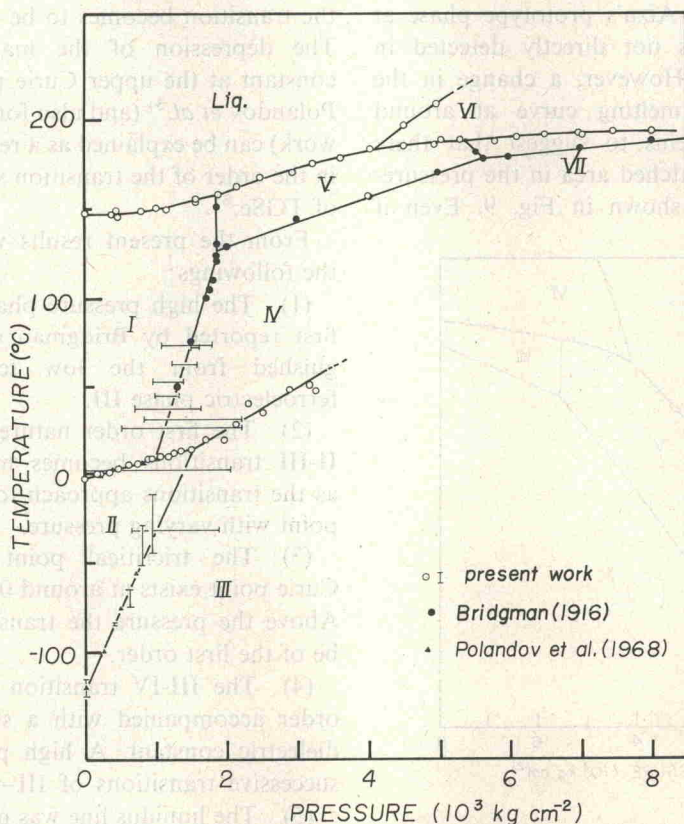


Fig. 8. Pressure-temperature phase diagram of  $\text{NH}_4\text{HSO}_4$ . Open circles and short bars indicate the present results. Points given by Bridgman<sup>2)</sup> and by Polandov *et al.*<sup>3)</sup> are indicated by solid circles and triangles, respectively.

tion temperature decreases with lowering pressure as seen in Fig. 8.

The present work reveals that there is a series of phase transitions in  $\text{NH}_4\text{HSO}_4$  at high pressures; Phase III  $\rightarrow$  Phase IV other than the atmospheric-pressure series of Phase II  $\rightarrow$  Phase I  $\rightarrow$  (The prototype structure;  $Pmmm$ ). The insignificant dielectric anomaly at the III-IV transition suggests that the structure of Phase IV is a slight modification of Phase III. In fact, Bridgman did not observe a volume change corresponding to the III-IV transition. This would be the reason why the extrapolation of the I-IV boundary tends to the lower Curie point of the II-III transition point at 1 atm. As to the crystal structure of Phase IV, only a powder X-ray study have been available.<sup>4)</sup> The reported unit cell dimension of Phase IV is just one third of that of Phase III given by Pepinsky *et al.* at 1 atm.<sup>1)</sup> However the space group determination for Phase IV should be postponed until a single crystal structure analysis is done.

The existence of Aizu's prototype phase at high pressures was not directly detected in the present work. However, a change in the curvature of the melting curve at around  $1 \times 10^3 \text{ kg cm}^{-2}$  seems to suggest that there is a phase in the hatched area in the pressure-temperature plane shown in Fig. 9. Even if

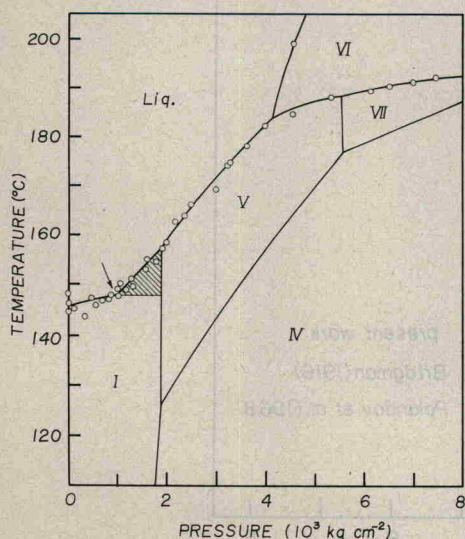


Fig. 9. Detailed view of the liquidus curve. A change in the curvature is shown by the arrow suggesting existence of a phase in the hatched area. The open circles show the results of DTA measurement.

there is a high pressure phase in this area the phase boundary between Phase I is so close to the melting that we can not separate the possible DTA signal from the latent heat of melting. At present, we would like to point out only the possibility of the existence of Aizu's prototype phase in a limited region in the cited area.

Recently tricritical points in ferroelectrics have attracted investigators' interest.<sup>8,12)</sup> A tricritical point in ferroelectric transition is described in the macroscopic electric field-temperature space, and then, a classical treatment is fully applicable. The order change of the transition at the upper Curie point in  $\text{NH}_4\text{HSO}_4$  provides a new example of tricritical point in ferroelectric crystal. The critical pressure of the tricritical point of the upper Curie point of  $\text{NH}_4\text{HSO}_4$  is not determined precisely, but the onset of the thermal hysteresis of the upper Curie point was seen at around  $0.6 \times 10^3 \text{ kg cm}^{-2}$ . Then, the tricritical point exists at this pressure, and above the pressure the transition becomes to be of the first order. The depression of the maximum dielectric constant at the upper Curie point reported by Polandov *et al.*<sup>3)</sup> (and also found in the present work) can be explained as a result of the change in the order of the transition similar to the case of TGSe.<sup>8)</sup>

From the present results we may conclude the followings:

(1) The high pressure phase IV which was first reported by Bridgman should be distinguished from the low temperature non-ferroelectric phase III.

(2) The first order nature in the I-IV and II-III transitions becomes more conspicuous as the transitions approach to the upper Curie point with varying pressure.

(3) The tricritical point for the upper Curie point exists at around  $0.6 \times 10^3 \text{ kg cm}^{-2}$ . Above the pressure the transition becomes to be of the first order.

(4) The III-IV transition is of the second order accompanied with a slight anomaly in dielectric constant. A high pressure series of successive transitions of III  $\rightarrow$  IV is suggested.

(5) The liquidus line was newly determined.

(6) Above about  $4 \times 10^3 \text{ kg cm}^{-2}$  a new pressure induced phase of Phase VI is found.