

a differential thermal analysis (DTA) was served for the detection of the I-II transition point at high pressures. The pressure-transmitting fluids used were 1:1 mixture of *iso*- and *n*-pentane (for the low temperature measurements) and silicone oil (for the high temperature measurements). Descriptions of the pressure system used were given elsewhere.<sup>3,4)</sup>

### §3. Results

#### 3.1 I-II transition

Figure 1 shows the DTA signal corresponding to the I-II transition at a pressure of 3.37 kbar. Because of relatively high rate of temperature change ( $\sim 20^\circ\text{C min}^{-1}$ ) large temperature hysteresis of  $\sim 6^\circ\text{C}$  was observed

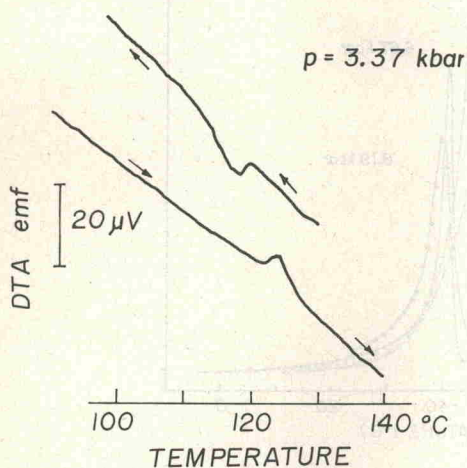


Fig. 1. DTA signal at the I-II transition of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  at 3.37 kbar.

during heating and cooling processes. In the present paper, the equilibrium I-II transition is presumably taken as the average point of the heating and cooling runs. The I-II transition point decreases with increasing pressure, and the relation between the I-II transition point and pressure can be approximated by a linear relation of  $T_c^{I-II} = T_c^0 + Kp$ . The parameters  $T_c^0$  and  $K$  are determined as  $139.8 \pm 0.1^\circ\text{C}$  and  $-5.76 \pm 0.03 \text{ deg kbar}^{-1}$ , respectively.

#### 3.2 II-III transition

At the II-III transition, a slight change in the temperature coefficient of the dielectric constant along the  $c^*$ -direction is seen.<sup>1)</sup> The break on the dielectric constant vs. temperature curve at the II-III transition point can be more clearly seen when one plots the inverse of the dielectric constant against temperature as shown in Fig. 2. In the figure, the II-III transition point is pointed by the vertical arrows for different pressures. The II-III transition point decreases with increasing pressure, but the relation between the transition point and pressure is not linear. If one expresses the relation by a quadratic function of  $p$  as  $T_c^{II-III} = T_c^0 + Kp + \gamma p^2$ , one gets the parameters as  $T_c^0 = -8.1 \pm 0.3^\circ\text{C}$ ,  $K = -3.7 \pm 0.2 \text{ deg kbar}^{-1}$ , and  $\gamma = -0.13 \pm 0.03 \text{ deg kbar}^{-2}$ . As seen in the pressure-temperature phase diagram of Fig. 6, the II-III phase boundary terminates at the II-III-VI triple point at  $p = 7.0 \pm 0.05 \text{ kbar}$ ,  $T = -40.5 \pm 0.5^\circ\text{C}$ .

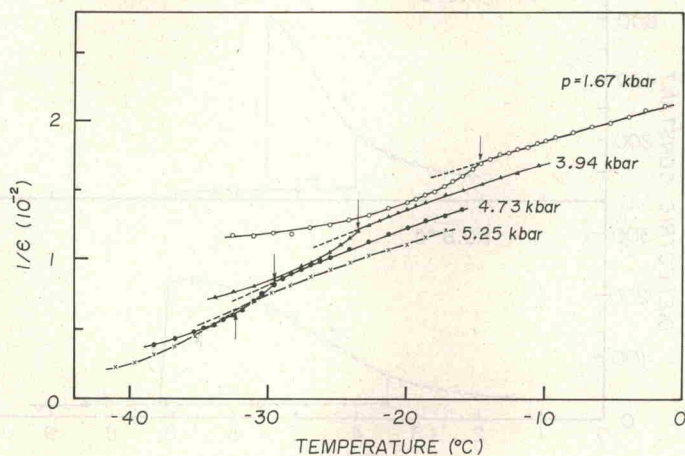


Fig. 2. Temperature dependence of the inverse dielectric constant along the  $c^*$ -direction of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  at various hydrostatic pressures. The anomaly at the II-III transition is indicated by the vertical arrows.

### 3.3 Pressure-induced phases (Phases VI, VII)

Figure 3 shows the dielectric constant vs. temperature curves at various hydrostatic pressures above 5 kbar. At 5.11 kbar two  $\lambda$ -type peaks of dielectric constant are seen; the fact indicates that there is a pressure-induced phase between the two peaks. The phase is denoted as Phase VI. As pressure further increases the peak at higher temperature shifts towards high temperature side, while the peak at lower temperature is masked by an appearance of the second pressure-induced phase which is called Phase VII.

Below about 5 kbar sharp peaks of dielectric constant which correspond to phase transitions are not observed. Ferroelectric activity has been found both for Phase VI and for Phase VII.<sup>2)</sup> Figure 4 shows the pressure dependence of the dielectric constant at  $-74.0 \pm 0.5^\circ\text{C}$  and  $-80.8 \pm 0.5^\circ\text{C}$ . Marked discontinuity and pressure hysteresis are found at the III-VII transition. Thus the transition from III to VII is clearly of the first order. As shown in Fig. 3, the VI-VII transition is also of the first order accompanied with a temperature hysteresis and a discontinuous jump in the dielectric

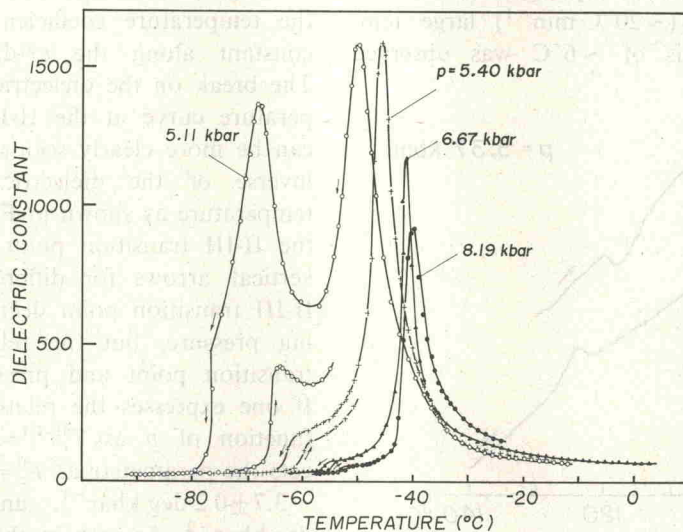


Fig. 3. Temperature dependence of the dielectric constant along the  $c^*$ -direction of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  at various hydrostatic pressures above 5 kbar.

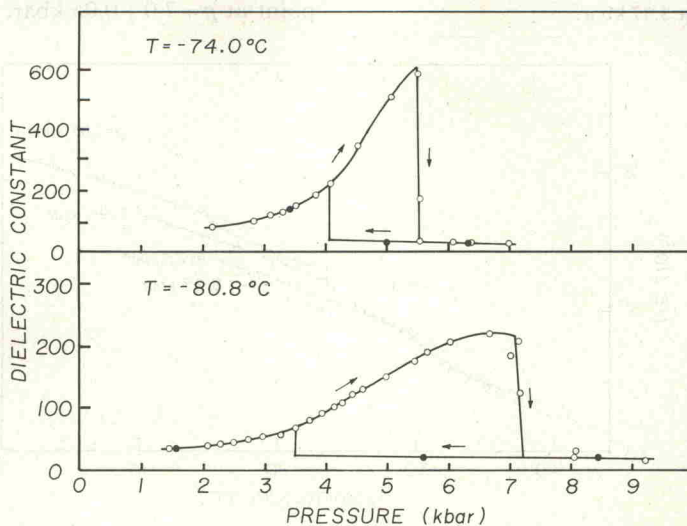


Fig. 4. Pressure dependence of the dielectric constant along the  $c^*$ -direction of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  at  $-74.0^\circ\text{C}$  (above) and  $-80.8^\circ\text{C}$  (below).