

Fig. 2. Temperature dependence of the dielectric constant of the (001)-plate of NH_4HSO_4 at $0.81 \times 10^3 \text{ kg cm}^{-2}$ (above) and $0.96 \times 10^3 \text{ kg cm}^{-2}$ (below). Open and closed figures indicate cooling and heating processes, respectively. The vertical arrows indicate the anomaly at the II-III transition point.

cm^{-2} corresponding to the II-III transition. On the pressure decreasing process, anomalies corresponding to the II-III and the I-II transitions do not appear down to 1 atm. This indicates that the high pressure phase of III is maintained as a metastable phase at 1 atm as a result of large pressure hysteresis of the transition. The large thermal and pressure hysteresis of the II-III transition makes the determination of the equilibrium phase boundary difficult.

3.2 Dielectric anomaly at the upper Curie point

Figure 4 shows the temperature dependence

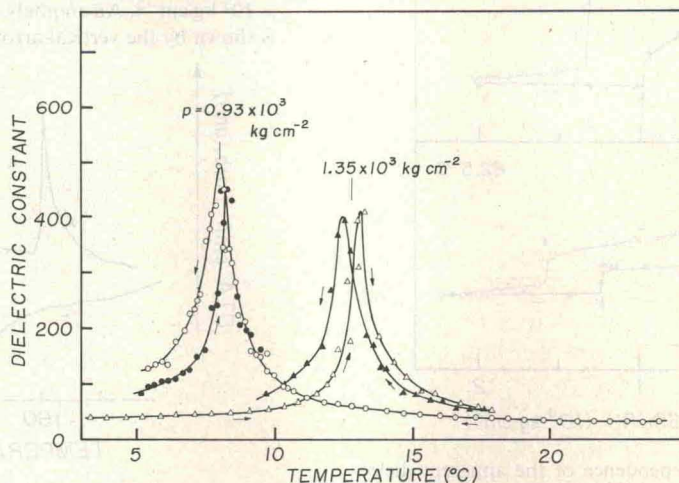


Fig. 4. Temperature dependence of the dielectric constant of the (001)-plate of NH_4HSO_4 at $0.93 \times 10^3 \text{ kg cm}^{-2}$ and $1.35 \times 10^3 \text{ kg cm}^{-2}$. Thermal hysteresis of the upper Curie point is shown.

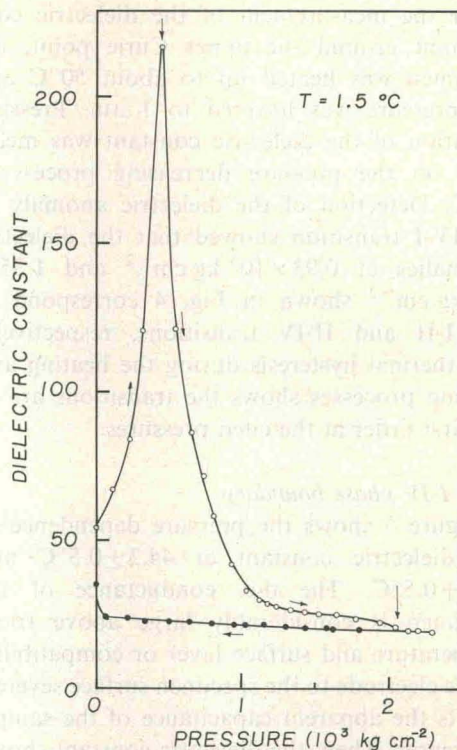


Fig. 3. Pressure dependence of the dielectric constant of the (001)-plate of NH_4HSO_4 at $T = 1.5^\circ\text{C}$. Open and closed figures indicate the pressure-increasing and the pressure-decreasing processes, respectively. The vertical arrows indicate the I-II and II-III transitions.

of the dielectric constant at pressures of $0.93 \times 10^3 \text{ kg cm}^{-2}$ and $1.35 \times 10^3 \text{ kg cm}^{-2}$. The measurements were carried out by keeping pressure within $\pm 2\%$ with a hand pump.

After the measurement of the dielectric constant around the upper Curie point, the specimen was heated up to about 50°C and the pressure was lowered to 1 atm. Pressure variation of the dielectric constant was measured on the pressure decreasing process at 50°C. Detection of the dielectric anomaly of the IV-I transition showed that the dielectric anomalies at $0.93 \times 10^3 \text{ kg cm}^{-2}$ and $1.35 \times 10^3 \text{ kg cm}^{-2}$ shown in Fig. 4 correspond to the I-II and II-IV transitions, respectively. The thermal hysteresis during the heating and cooling processes shows the transitions are of the first order at the cited pressures.

3.3 I-IV phase boundary

Figure 5 shows the pressure dependence of the dielectric constant at $44.3 \pm 0.5^\circ\text{C}$ and $62.5 \pm 0.5^\circ\text{C}$. The d.c. conductance of the specimen is considerably large above room temperature and surface layer or compatibility of the electrode to the specimen surface severely affects the apparent capacitance of the sample condenser. Then, the dielectric constant shown in Fig. 5 should be considered to be an apparent one. However in spite of the lack of reproducibility in the absolute value of the apparent dielectric constant one may observe a discontinuous jump on the curves as shown

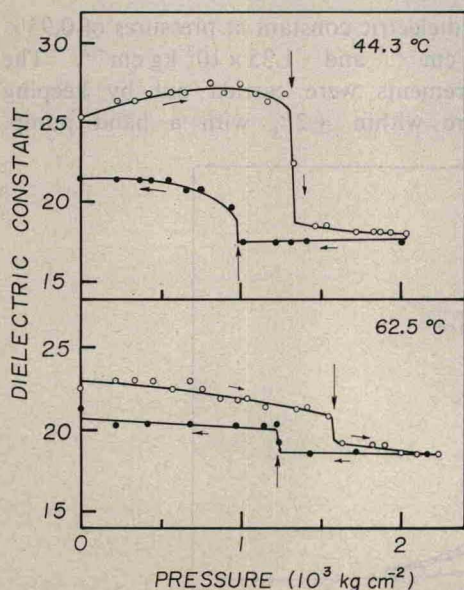


Fig. 5. Pressure dependence of the apparent dielectric constant of the (001)-plate of NH_4HSO_4 at 44.3°C and at 62.5°C . The discontinuous jump at the I-IV transition is indicated by the vertical arrow.

by the vertical arrows for the I-IV transition. The pressure hysteresis of the I-IV transition is large and becomes remarkable as temperature approaches to the upper Curie point.

3.4 III-IV phase boundary

Above about $1.6 \times 10^3 \text{ kg cm}^{-2}$ peaks of dielectric constant were not found at the extension line of the upper Curie temperature. Instead we found a slight change in the temperature coefficient of the dielectric constant as shown in Fig. 6. We tentatively assigned the dielectric anomaly to the III-IV transition. The results indicate that the high pressure phase found by Bridgman (Phase IV) is not identical with the low temperature non-ferroelectric phase of III.

3.5 Determination of the liquidus line

Figure 7 shows the DTA signal which cor-

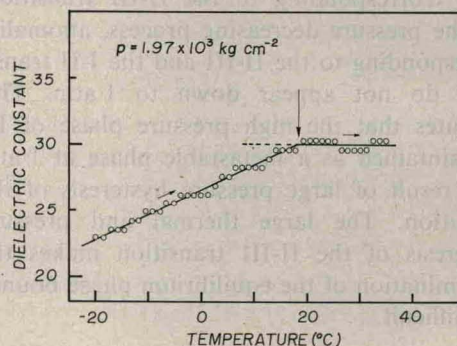


Fig. 6. Temperature dependence of the dielectric constant of the (001)-plate of NH_4HSO_4 at $1.97 \times 10^3 \text{ kg cm}^{-2}$. An anomaly at the III-IV transition is shown by the vertical arrow.

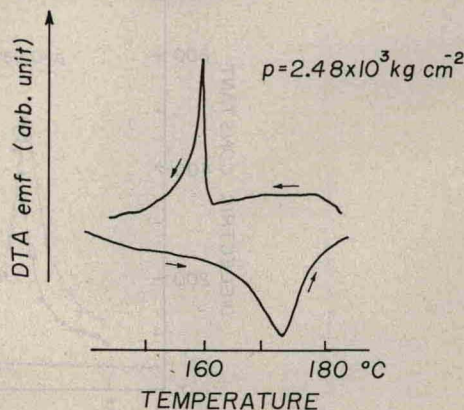


Fig. 7. DTA signal at the melting of NH_4HSO_4 at $p = 2.48 \times 10^3 \text{ kg cm}^{-2}$.