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## Changes in the Thermodynamic Character of the $\text{NH}_4\text{Cl}$ Order-Disorder Transition at High Pressures\*

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Variations in the length  $L$  of an  $\text{NH}_4\text{Cl}$  crystal in the vicinity of its order-disorder transition line have been determined with a capacitance method. At low pressures, there is a small first-order discontinuity  $\Delta L$  superimposed on a  $\lambda$ -like variation in  $L$ . At a "critical point" near 255.75°K and 1493 bar,  $L$  varies continuously but  $\kappa_T$  and  $\alpha$  appear to diverge. At higher pressures, the variation in  $L$  at the transition becomes progressively more gradual.

The order-disorder transition in  $\text{NH}_4\text{Cl}$ , which involves the relative orientations of the tetrahedral  $\text{NH}_4^+$  ions in a CsCl-type cubic structure, is in

many ways analogous to the ferromagnetic transition in a compressible Ising lattice. In the case of  $\text{NH}_4\text{Cl}$ , mechanical variables play an important

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role: The disordered crystal is relatively soft, there is an anomalous volume contraction associated with the ordering process, and the transition temperature is a sensitive function of pressure. In this paper we shall report measurements of the length of an  $\text{NH}_4\text{Cl}$  single crystal which indicate that the detailed character of the order-disorder transition is different at various points along the transition line.

A variety of measurements at 1 atm indicate that there is hysteresis in the transition temperature and small finite discontinuities superimposed on the expected  $\lambda$ -like behavior.<sup>1-5</sup> In particular, there is a small latent heat<sup>4</sup> and a discontinuous change in the length of a single crystal.<sup>5</sup> Thus, a thermodynamic instability leading to a first-order transition is now well established at 1 atm. There are several high-pressure investigations which indicate that the transition becomes less sharp as the pressure is increased.<sup>2,6,7</sup> Of these, ultrasonic velocity measurements on large single crystals<sup>2</sup> provide the most reliable equilibrium data, but the experimental points are somewhat sparse in the immediate vicinity of the transition line. None of these previous studies is really definitive in establishing the changing character of the transition along the transition line. With this in mind, we have designed a high-precision capacitance cell to measure small changes in the length of a single crystal at high pressures.

The experimental arrangement is such that changes in the length  $L$  of a single-crystal sample are directly reflected in changes in the gap  $d_s$  between the plates of a three-lead capacitor. A transformer ratio-arm bridge (General Radio 1615A) and a lock-in detector (PAR 121) are used to measure the capacitance  $C_s = \epsilon G/d_s$  of this "sample" cell. The geometric factor  $G$  is essentially equal to the area of the parallel plates but also involves fringing field corrections which are dependent on the details of the guard ring. In order to determine the pressure dependence of  $d_s$  (and thus of  $L$ ), one must take account of the considerable variation in the dielectric constant  $\epsilon$  of the argon gas used to generate the hydrostatic pressure. For this purpose, we have constructed a reference cell with the same radial geometry as the sample cell and with a gap  $d_R$  which is determined by a fused silica spacer. Our method involves measuring the sample-cell capacitance  $C_s$  and the reference-cell capacitance  $C_R$  under identical conditions of pressure and temperature. It follows that the experimental ratio  $C_R/C_s$  is essentially equal to  $d_s/d_R$ , where  $d_R$  is a known slowly varying function of  $p$  and  $T$ .

Our measurements were made on  $\text{NH}_4\text{Cl}$  single crystals with lengths  $L \approx 1.00$  cm at  $20^\circ\text{C}$  and 1 atm. We used gaps  $d_s \approx 0.1$  cm and  $d_R \approx 0.2$  cm between capacitor plates 1.2 cm in diameter;

thus the nominal capacitance values were 1 and 0.5 pF, respectively. Since these capacitance values could be determined to within  $\pm 10^{-5}$  pF, changes in the length  $L$  as small as  $10^{-6}$  cm could be detected.

Isothermal changes in the length of two different  $\text{NH}_4\text{Cl}$  single crystals have been measured as a function of pressure from 0 to 3.7 kbar at nine different temperatures in the range between 250 and  $270^\circ\text{K}$ . Temperature stability of  $\pm 3$  mdeg could be maintained for long periods, and pressure changes as small as 0.3 bar could be measured with a calibrated manganin resistance gauge. In addition to these isothermal runs, isobaric measurements were made at 1636 and 2841 bar on one of the crystals. During these measurements, the pressure was held constant to within  $\pm 0.8$  bar (within  $\pm 0.3$  bar in the immediate vicinity of the transition). The absolute accuracies of the temperature and pressure determinations were estimated to be  $\pm 0.05^\circ\text{K}$  and  $\pm 3$  bar, respectively.

The striking change in the detailed character of the transition at different points along the order-disorder transition line is the most interesting new result from our work. To illustrate this feature, the variation in  $L$  in the immediate vicinity of the transition is shown in Figs. 1 and 2 for four selected isotherms and in Fig. 3 for the two high-pressure isobars.

Curve (a) in Fig. 1 was obtained at  $250.04^\circ\text{K}$ , the lowest temperature studied. No hysteresis was observed, but there is a discontinuous change in  $L$  at the transition.<sup>8</sup> However, the first-order change

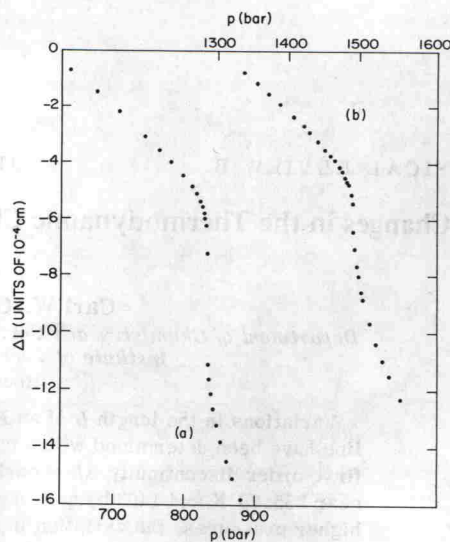


FIG. 1. Isothermal variation of the length  $L$  of an  $\text{NH}_4\text{Cl}$  single crystal. For curve (a),  $\Delta L = L(p) - L(600 \text{ bar})$  for  $L$  values at  $250.04^\circ\text{K}$ . For curve (b),  $\Delta L = L(p) - L(1300 \text{ bar})$  for  $L$  values at  $255.75^\circ\text{K}$ .