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Changes in the Thermodynamic Character of the NH_4Cl Order-Disorder Transition at High Pressures*

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Variations in the length L of an NH_4Cl 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 ΔL superimposed on a λ -like variation in L . At a "critical point" near 255.75°K and 1493 bar, L varies continuously but κ_T and α appear to diverge. At higher pressures, the variation in L at the transition becomes progressively more gradual.

The order-disorder transition in NH_4Cl , which involves the relative orientations of the tetrahedral 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 NH_4Cl , 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 NH_4Cl 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 λ -like behavior.¹⁻⁵ In particular, there is a small latent heat⁴ and a discontinuous change in the length of a single crystal.⁵ 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.^{2,6,7} Of these, ultrasonic velocity measurements on large single crystals² 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 ϵ 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 NH_4Cl single crystals with lengths $L \approx 1.00$ cm at 20 °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 NH_4Cl 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 °K. Temperature stability of ± 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 ± 0.8 bar (within ± 0.3 bar in the immediate vicinity of the transition). The absolute accuracies of the temperature and pressure determinations were estimated to be ± 0.05 °K and ± 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 °K, the lowest temperature studied. No hysteresis was observed, but there is a discontinuous change in L at the transition.⁸ However, the first-order change

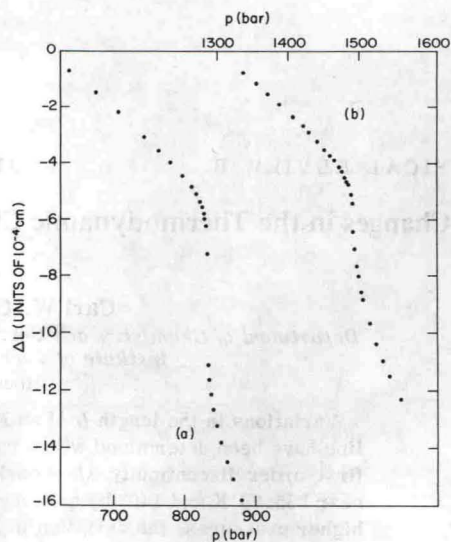


FIG. 1. Isothermal variation of the length L of an NH_4Cl single crystal. For curve (a), $\Delta L = L(p) - L(600 \text{ bar})$ for L values at 250.04 °K. For curve (b), $\Delta L = L(p) - L(1300 \text{ bar})$ for L values at 255.75 °K.

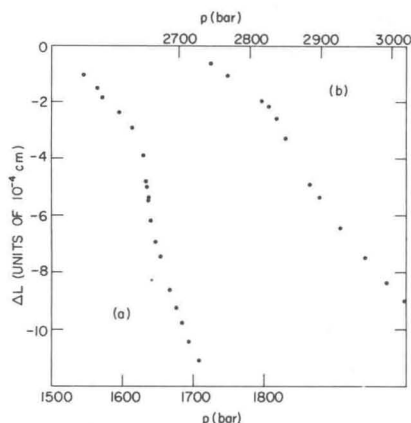


FIG. 2. Isothermal variation of the length L of an NH_4Cl single crystal. For curve (a), $\Delta L = L(p) - L(1500 \text{ bar})$ for L values at 256.94°K . For curve (b), $\Delta L = L(p) - L(2700 \text{ bar})$ for L values at 266.37°K .

$\Delta L/L \approx 3.8 \times 10^{-4}$ observed at 833 bar is considerably smaller than the discontinuity $\Delta L/L \approx 12 \times 10^{-4}$ at 1 atm.^{1,5} It should be noted that in both cases the first-order change in length at the transition point is only a fraction of the total anomalous variation associated with the ordering. The over-all length contraction due to ordering extends quite far into the ordered phase and amounts to $\approx 0.37\%$ for the 1-atm isobar. Although the crystal is less compressible at high pressures, the over-all anomaly still amounts to $\approx 0.15\%$ for the 250°K isotherm. The general behavior of L as a function of p and T over a wide range in these variables will be discussed elsewhere,⁹ but it is worthwhile to point out that these variations correspond quite closely to those anticipated from measurements of the shear stiffness c_{44} .¹⁰ Finite discontinuities in L were also observed in isotherms at 251.40 and 254.11°K . In the latter case, the transition occurs at 1303 bar and the first-order change $\Delta L/L$ amounts to only 1.7×10^{-4} .

Curve (b) in Fig. 1 was obtained at 255.75°K and represents the most nearly "critical isotherm" that we have observed. In this case, it is very difficult to determine whether there is a small discontinuity with $\Delta L/L$ less than 10^{-4} or a continuous variation in L with $\kappa_T \equiv -3L^{-1}(\partial L/\partial P)_T$ becoming infinite at the transition pressure of 1493 bar. Five isotherms obtained at higher temperatures (256.94 , 257.64 , 260.00 , 266.37 , and 269.93°K) were all characterized by a continuous variation in L which became more and more gradual in the transition region as the temperature was increased. Figure 2 illustrates this trend by showing the behavior observed at 256.94 and 266.37°K . Note that the 256.94°K isotherm definitely implies a finite maximum in κ_T at the transition pressure of 1633 bar. Thus the "critical point" (i.e., the point on the transition

line above which L varies continuously) must lie below 256.94°K and 1633 bar and is probably quite close to 255.75°K and 1493 bar.

The progressive change in the character of the transition is also indicated by the two isobars shown in Fig. 3. In the case of curve (a) ($p = 1636 \text{ bar}$), the order-disorder transition line was crossed just above the "critical point." It can be seen that L is continuous through the transition and that $\alpha \equiv 3L^{-1} \times (\partial L/\partial T)_P$ becomes very large but not infinite at a transition temperature of 256.96°K . Curve (b) in Fig. 3 was obtained at 2841 bar and shows the much more gradual variation which is observed near the transition temperature of 266.42°K .

In the past few years, there has developed an increasing interest in statistical theories of the phase transition in compressible Ising lattices. Experimental results on NH_4Cl have been analyzed previously in terms of an Ising model in which the interaction energy J depends on the average lattice parameter.¹¹ For this model, a mechanical instability ($1/\kappa_T < 0$) and a first-order transition will occur whenever the specific heat exceeds a critical value which depends on the compressibility of the disordered lattice. Since high-pressure differential-thermal-analysis (DTA) measurements on NH_4Cl suggest that the peak value of C_p diminishes significantly as one moves up along the transition line,⁷ it might be imagined that this model could account for the present experimental results. However, there are theoretical objections¹² to this and other related models in which J depends only on the average lattice spacing. Very recently, it has been shown^{13,14} that mechanical instability does not occur if the lattice parameter is allowed to fluctuate (i.e., the lattice is allowed to adjust itself locally to the internal stresses caused by the fluctuating spin system). For such models, κ_T undergoes a rapid variation near the transition point but never exceeds a maximum value of $3/2p$.

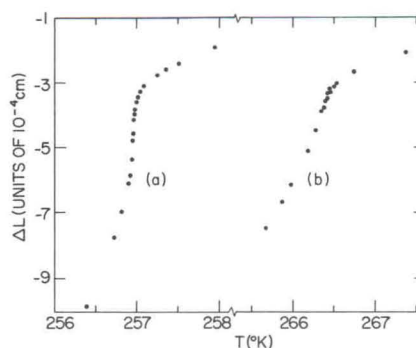


FIG. 3. Isobaric variation of the length L of an NH_4Cl single crystal. For curve (a), $\Delta L = L(T) - L(260^\circ\text{K})$ for L values at 1636 bar. For curve (b), $\Delta L = L(T) - L(270^\circ\text{K})$ for L values at 2841 bar.

However, the theoretical situation is unclear with respect to the possibility of first-order transitions. The theory presented by Wagner and Swift¹³ does not predict a first-order transition, whereas the model of Baker and Essam¹⁴ exhibits a first-order transition related to a thermal instability ($1/C_p < 0$). In the latter case, κ_T attains its upper bound of $3/2\rho$ at the point of instability. Since this value is very

large at low pressures, it would be quite difficult to distinguish experimentally between this transition and one due to a mechanical instability. Although the Baker-Essam model has been applied quite successfully to the analysis of 1-atm data for β -brass, it is not yet clear whether it can account for a rapid change in the character of a transition with pressure.

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