FIG. 2. Isothermal variation of the length L of an NH$_4$Cl single crystal. For curve (a), $\Delta L = L(p) - L(1500$ bar$)$ for L values at 256.94 °K. For curve (b), $\Delta L = L(p) - L(2700$ bar$)$ for L values at 266.37 °K.

$\Delta L/L \simeq 3.8 \times 10^{-4}$ observed at 833 bar is considerably smaller than the discontinuity $\Delta L/L \simeq 12 \times 10^{-4}$ 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) ($p = 1636$ 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$_4$Cl 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$_4$Cl 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 objections[12] 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 $3/2p$.
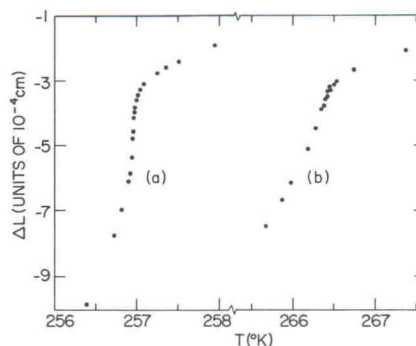

FIG. 3. Isobaric variation of the length L of an NH$_4$Cl single crystal. For curve (a), $\Delta L = L(T) - L(260$ °K$)$ for L values at 1636 bar. For curve (b), $\Delta L = L(T) - L(270$ °K$)$ for L values at 2841 bar.

However, the theoretical situation is unclear with respect to the possibility of first-order transitions. The theory presented by Wagner and Swift[13] does not predict a first-order transition, whereas the model of Baker and Essam[14] exhibits a first-order transition related to a thermal instablity ($1/C_p < 0$). In the latter case, κ_T attains its upper bound of $3/2p$ 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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