Notice also the considerable difference between the shape of the c_{11}-vs-T curve at constant pressure and at constant volume.

Equation (6) would seem to predict that $1/\beta^T$ could become negative near the lambda point (where $C_I \to \infty$). However, the crystal becomes unstable as $1/\beta^T \to 0$ and should undergo a first-order transition. Details of this kind of behavior are given in Paper I, where instability and hysteresis are predicted for an Ising model. Our data indicate that $1/\beta^S$ does not vanish at any temperature, but precise work is very difficult in the critical region due to the extremely high attenuation. In any case, the lack of very accurate thermal expansion and specific heat data in the immediate region of the critical point makes it impossible to calculate $1/\beta^T$ from $1/\beta^S$. Therefore, we do not know whether $1/\beta^T$ vanishes or not. However, the shear constants (especially c_{44}) are sensitive functions of the molar volume and can be viewed as probes to study the behavior of the volume near the lambda point. Since there is no excess attenuation associated with the shear waves, it is possible to follow their behavior throughout the entire transition region both on warming and cooling the sample.

Both c_{44} and C' show a definite hysteresis of $0.9° \pm 0.2°$K at 1 atm, and for c_{44} this has been followed as a function of pressure (see the inset on Fig. 1). In addition, our shear data strongly suggest a sluggish first-order transition in the critical region. For points taken at temperatures more than 1°K away from T_λ and at pressures more than 100 bar away from p_λ, equilibrium was achieved within about 15 min after the temperature or pressure was adjusted. In the immediate vicinity of a critical point, very slow changes in velocity were still observed 45 min after the temperature or pressure was adjusted, as would be expected in a metastable region. Also the changes in c_{44} and C' in this narrow hysteresis region are extremely abrupt, even when compared with the very rapid variations observed in the ordered phase near the transition line. (See Figs. 5 and 6.) The presence of hysteresis and the very abrupt changes in velocities near T_λ are perhaps the most significant features of our shear data at 1 atm.

This same sort of behavior has also been observed in the temperature dependence of the volume of powdered samples of NH_4Cl. Dinichert[25] carried out a very careful x-ray measurement of the unit cell dimensions in the critical region, while Thomas and Staveley[26] measured the volume directly. In both cases, a hysteresis loop was observed with a temperature width of about 0.4°K. At the transition temperature, on cooling and warming, a very sharp volume change of $\Delta V/V = 4.7 \times 10^{-3}$ was observed. Both these authors proposed theories for this hysteresis, which are not discussed here except to point out that both theories treat the transition as first order.

[25] P. Dinichert, Helv. Phys. Acta **15,** 462 (1942).

[26] D. G. Thomas and L. A. K. Staveley, J. Chem. Soc. **1951,** 1420.

The discussion given in Paper I shows how the usual ideas of order–disorder transitions based on Ising models can be reconciled with the notion of a first-order transition and hysteresis. The qualitative behavior of ammonium chloride is in excellent agreement with the predictions of Paper I, and we shall attempt a more quantitative comparison by making an approximate calculation of the hysteresis predicted for a three-dimensional Ising model. Let us begin in terms of the two-dimensional case and refer to Fig. 1 of Paper I. On the Ising isotherm T_5 we have marked the point D where the tangent is parallel to the disordered-lattice isotherm; on the disordered-lattice isotherm T_5 we have marked the point C such that the line DC is parallel to the area axis. We notice that to a rough approximation (valid for a small range of temperatures near the critical point) the Ising isotherms are related to each other by a translation parallel to the σ axis. The same is valid in a more general sense for the disordered-lattice isotherms. In this approximation, all points on the spin isotherms where the tangent is equal to the slope of the disordered-lattice isotherm are on a straight line parallel to the σ axis. If T_5 is the temperature of the upper mechanical instability point, and T_3 is that of the lower one, then $\Delta T = T_5 - T_3$ can be determined from the condition $\sigma_D - (d\sigma_D/dT)\Delta T = \sigma_{3'} = \sigma_C - \sigma_C \alpha_{dl} \Delta T$. This gives

$$\Delta\sigma' = [\sigma_C \alpha_{dl} - (d\sigma_D/dT)]\Delta T,$$

where $\Delta\sigma'$ is defined as $\sigma_C - \sigma_D$. But $d\sigma_D/dT \simeq d\sigma_5/dT$ and σ_C will be numerically quite close to σ_5, therefore

$$\Delta T \simeq \frac{\Delta\sigma'}{\sigma_5} \Big/ \left(\alpha_{dl} - \frac{1}{\sigma_5}\frac{d\sigma_5}{dT}\right). \tag{10}$$

We define also $\Delta\sigma = \sigma_{5'} - \sigma_5$; thus $\Delta\sigma/\sigma_5$ is the relative area expansion of the crystal when the first-order transition takes place on warming. For a three-dimensional crystal, Eq. (10) becomes

$$\Delta T \simeq \frac{\Delta v'}{v_\lambda} \Big/ \left[\alpha_{dl} - \frac{1}{v_\lambda}\left(\frac{dv}{dT}\right)_\lambda\right], \tag{11}$$

and the relative volume change associated with the first-order transition is denoted by $\Delta v/v_\lambda$.

Now we wish to calculate ΔT and $\Delta v/v_\lambda$ for ammonium chloride. We know $(1/v_\lambda)(dv/dT)_\lambda$ experimentally. The value for α_{dl} in the critical region can be extrapolated from the temperature dependence of the thermal expansion in the disordered phase far away from the lambda point. To evaluate $\Delta v'/v_\lambda$ and $\Delta v/v_\lambda$ we use Fisher's theoretical expressions for the specific heat "per site" for a simple-cubic lattice,[27] which are based on an assumed logarithmic singularity at the critical point. Integrating his expressions above and below the critical temperature with respect to $H \equiv J/kT$ we obtain the internal energy "per site" as a function of H. From Eq. (6) of Paper I we get equations for p_I

[27] M. E. Fisher, Phys. Rev. **136,** A1599 (1964).

around the critical point. Using the known variation of T_λ (and thus J) with v, one can plot on a p–V diagram the Ising isotherm at 241.5°K and the disordered-lattice isotherm based on the extrapolated value at 241.5°K of the isothermal compressibility $\beta_{dl}{}^T$. (We used $\beta_{dl}{}^T = 5.9\times10^{-12}$ cm^2 dyn^{-1}.) From this plot we determined $\Delta v/v_\lambda = 0.78\times10^{-3}$ and $\Delta v'/v_\lambda = 1.15\times10^{-4}$. Substituting this latter value into Eq. (11) and letting $(1/v_\lambda)(dv/dT)_\lambda = -4.17\times10^{-4}$ deg^{-1} and $\alpha_{dl} = 1.11\times10^{-4}$ deg^{-1}, we find a hysteresis ΔT of 0.22°K.

The predicted value of $\Delta v/v_\lambda$ (0.78×10^{-3}) is smaller than the experimental value of 4.7×10^{-3}. This could mean that the singularity at the critical temperature is stronger than a logarithmic singularity, which is certainly possible because a logarithmic singularity is the weakest type. However, we must remember that Fisher's expressions are not exact and Eq. (11) involves several approximations; thus we should not expect better than order-of-magnitude agreement. Since the predicted value of $\Delta v/v_\lambda$ is too small, $\Delta v'/v_\lambda$ and ΔT should also be too small. If we use the experimental $\Delta v/v_\lambda$ value as a guide for correcting our prediction of ΔT, a new predicted value of 1.3°K would be obtained. Thus the theoretical maximum value of the temperature hysteresis should lie in the range 0.2° to 1.3°K, in reasonable agreement with the observed values which range between 0.4° and 0.9°K. Although this comparison between theory and experiment is difficult and approximate, it strongly supports the validity of the Ising model defined in Paper I as a description of the ordering process in ammonium chloride.

In summary, we have shown that there is agreement over a wide range of temperatures between the constant-volume elastic constants of NH_4Cl single crystals and the predicted elastic behavior of a compressible Ising model and in addition that the predicted instability and hysteresis at temperatures very close to the lambda point does occur. Ammonium chloride is a favorable case for observing such effects. It is interesting to speculate that the same effects may be present on a much smaller scale near order–disorder points in other, less compressible crystals.