Order–Disorder Phenomena. III. Effect of Temperature and Pressure on the Elastic Constants of Ammonium Chloride*

CARL W. GARLAND AND RÉMI RENARD†

Department of Chemistry, Research Laboratory of Electronics, and Center for Materials Science and Engineering
Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received 18 August 1965)

The adiabatic elastic constants of single-crystal ammonium chloride have been measured at 20 Mc/sec as functions of temperature and pressure in the region of the lambda transition. At atmospheric pressure, data were obtained over the range of temperature from 150° to 320°K. At five temperatures, evenly spaced between 250° and 310°K, measurements were made as the pressure was varied from 0 to 12 kbar. The values at 300°K and atmospheric pressure are: $c_{11}=3.815$, $c_{44}=0.8878$, $C'=1.4698$, in units of 10^{11} dyn cm^{-2}. A hysteresis of the critical temperature, equal to ~ 0.9°K at atmospheric pressure, was observed; this hysteresis disappears rapidly as the hydrostatic pressure is increased. The results are in good agreement with those predicted for a compressible Ising model. In particular, it is concluded that the order–disorder transition in ammonium chloride is not of a simple lambda type. It is proposed that NH$_4$Cl is unstable in the immediate vicinity of its critical point and undergoes a first-order transition.

INTRODUCTION

AMMONIUM chloride undergoes a lambda transition of the order–disorder type which involves the relative orientations of the tetrahedral ammonium ions in a CsCl-type structure. As a result of electrostatic attractions, the most stable orientation of the NH$_4^+$ ion in the cubic unit cell is for the hydrogen atoms to point toward the nearest-neighbor Cl$^-$ ions. Thus there are two possible positions for the ammonium ion. In the completely ordered state, all NH$_4^+$ tetrahedra have the same relative orientation with respect to the crystallographic axes (at least for a given domain); in the completely disordered state, the orientations are random with respect to these two positions.[1] Strictly speaking, the NH$_4^+$ ions librate about their equilibrium positions in both the ordered and disordered state.[2]

In many respects NH$_4$Cl is an ideal crystal for studying cooperative order–disorder phenomena. The orientational ordering is of a simple kind, completely analogous to the spin ordering of a simple-cubic ferromagnet in zero external field. The difference in interaction energy between parallel and antiparallel NH$_4^+$ ions is very largely due to octopole–octopole terms between nearest NH$_4^+$ neighbors,[3] and thus the Ising model is quite a good approximation for a NH$_4$Cl lattice. Furthermore, the ordering process should have little effect on the dynamics of such an ionic lattice. For these reasons, the theory developed in the preceding papers[4,5] (called Papers I and II) for the mechanical behavior of an Ising lattice should be directly pertinent to an interpretation of the elastic properties of ammonium chloride.
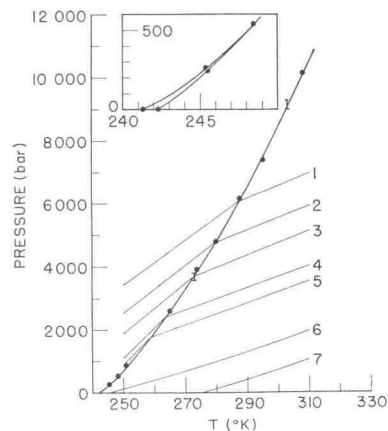

FIG. 1. Phase diagram for NH$_4$Cl. The high-pressure, low-temperature field corresponds to the ordered phase. The data points were obtained from the abrupt "break" in the ultrasonic shear velocities at the λ transition point (see Figs. 8 and 9); the vertical bars indicate static volume measurements of Bridgman.[17] The light lines numbered 1 through 7 represent isochores at various volumes (see legend of Fig. 5 for values of V_i).

The present paper reports the results of a variety of ultrasonic velocity measurements which have been made on single-crystal ammonium chloride. Both longitudinal and transverse acoustic waves were studied over a wide range of temperature (150°–320°K) and pressure (0 to 12 kbar). In these investigations special emphasis was given to the "anomalous" behavior near the lambda transition. As shown in Fig. 1, the transi-

[1] H. A. Levy and S. W. Peterson, Phys. Rev. **83**, 1270 (1951), **86**, 766 (1952).

[2] E. L. Wagner and D. F. Hornig, J. Chem. Phys. **18**, 296, 305 (1950).

[3] C. W. Garland and J. S. Jones, J. Chem. Phys. **41**, 1165 (1964).

[4] C. W. Garland and R. Renard, J. Chem. Phys. **44**, 1120 (1966)

[5] R. Renard and C. W. Garland, J. Chem. Phys. **44**, 1125 (1966).

tion temperature is a fairly strong function of pressure, increasing from $\sim242°K$ at 1 atm to $\sim308°K$ at 10 kbar. Ultrasonic velocities at a constant pressure of 1 atm have been measured previously[6] by a pulse-echo method as a function of frequency and temperature, and no dispersion was observed between 5 and 55 Mc/sec. The temperature dependence at 1 atm has been restudied, and the pressure dependence of the velocities were measured at five fixed temperatures spaced between 250° and 308°K. Thus, we have very precise velocity data on both the ordered and disordered phases. These experimental data will permit us to separate the effects on the elastic properties of changes in volume and changes in temperature from the effects due to changes in ordering (at constant V and T).

The results presented below are given in terms of the variation of the three adiabatic elastic constants c_{11}, c_{44}, and C', which can be obtained directly from the experimental sound velocities. Third-order elastic constants are not used, and for pressures above 1 atm the quantities c_{11}, c_{44}, and C' are "effective" elastic constants.[7] The relations between the ultrasonic velocities and the elastic constants of a cubic crystal are well known:

$$c_{11} = \rho U_l^2, \tag{1}$$

where ρ is the mass density of the crystal and U_l is the velocity of a longitudinal sound wave traveling in the [100] direction;

$$c_{44} = \rho U_t^2, \tag{2}$$

where U_t is the velocity of a transverse wave traveling in the [100] direction and polarized in any direction;

$$C' = (c_{11} - c_{12})/2 = \rho U_{t'}^2, \tag{3}$$

where $U_{t'}$ is the velocity of a transverse wave traveling in the [110] direction and polarized perpendicular to the [001] axis;

$$c_{11} + c_{44} - C' = \rho U_{l'}^2, \tag{4}$$

where $U_{l'}$ is the velocity of a longitudinal wave traveling in the [110] direction. Values of $U_{l'}$ were measured only at 1 atm as a check on the internal consistency of the data.

EXPERIMENTAL WORK

In order to achieve both a very good absolute accuracy and an excellent relative precision for all the velocities, measurements were made with the pulse-superposition technique. This method, developed by McSkimin,[8,9] involves applying identical external pulses to the sample at a repetition rate $N = 1/t$ such that t is approximately equal to some integral multiple (p) of the time delay between successive echoes. When the value of t is slowly varied, the amplitude of the superposed echoes will oscillate between a maximum value corresponding to all echoes being in phase and a minimum value corresponding to successive echoes being out of phase. The general expression for an *in-phase* value of t is given by[8,9]

$$t = p\delta - p\gamma/360f + n/f, \tag{5}$$

where $t(=1/N)$ and the rf carrier frequency f are known by direct measurement, p is an exact integer determined by the mode of operation, and $\delta = 2L/U$ is the true round-trip transit time for a plane sound wave with velocity of propagation U traveling back and forth inside a sample of length L. In order to determine δ one must evaluate γ, the phase shift (in degrees) associated with the reflection of the sound wave at the transducer+seal end of the sample, and the integer n which indicates which of the in-phase conditions is involved. (For $n=0$, the first rf peaks of all the superposed echoes coincide; for $n=\pm1$ the first peaks of successive superposed echoes are displaced by one period of the carrier frequency, etc.) The value of γ can be calculated[8] from the acoustical impedances of the sample, seal, and transducer, the thicknesses of the seal and transducer, and the frequency f. All of these quantities are known with sufficient accuracy except the seal thickness. In order to determine the seal thickness and the n values, in-phase values of t were determined at two different frequencies—f_R, the resonance frequency of the transducer, and a second frequency between $0.90f_R$ and $0.95f_R$. Although the pulse-superposition method is experimentally and computationally more difficult than the pulse-echo method, it has the great advantage of involving the measurement of a frequency rather than of a time delay and of allowing one to evaluate quantitatively the effect of reflections. Further refinements of this method are given in a recent paper by McSkimin.[10] The only disadvantage of this method for the present investigation is the fact that it cannot be used under conditions where the sample has a very large ultrasonic absorption.

All of the measurements were carried out in the $p=1$ mode of operation since this is the best method for the unambiguous determination of the $n=0$ value of t. In order to observe the superposed echo signals in this case it is necessary to interrupt the sequence of external pulses. This is easily achieved by using the A^+ gate of a Tektronix 545A oscilloscope to block the generation of external pulses during the time of the A sweep. A block diagram of the electronic circuit is shown in Fig. 2; although equivalent to the original McSkimin setup, the present apparatus involves differ-

[6] C. W. Garland and J. S. Jones, J. Chem. Phys. **39**, 2874 (1963).

[7] R. N. Thurston, J. Acoust. Soc. Am. **37**, 348 (1965).

[8] H. J. McSkimin, J. Acoust. Soc. Am. **33**, 12 (1961).

[9] H. J. McSkimin and P. Andreatch, J. Acoust. Soc. Am. **34**, 609 (1962); J. Appl. Phys. **34**, 651 (1963).

[10] H. J. McSkimin, J. Acoust. Soc. Am. **37**, 864 (1965).