References and Notes
[10] The deviation from a straight line exhibited by Edwards and Woodbury appear to be much too large to permit of experimental error. If these deviations are real, they might be attributed to quantum corrections to the law of corresponding states (I. de Boer, Physica 14, 139-149 (1948); J. de Boer and R. J. Landau, Physica 14, 590 (1948), and similar behavior might be observed in He.
[11] Such appears to be the case (see paper by R. H. Norman in this conference).
[12] The line in the figure actually has a finite intercept of -4.6 millidegrees on the abcissa. This may indicate flattening of the existence curve close to the critical point, or may be the result of errors in the measured temperature. In any case, the result is clear that the transition has a CsCl-type cubic structure both above and below the critical temperature; thus the transition has a CsCl-type cubic structure both above and below the critical temperature.
[13] The authors are extremely grateful to Laszlo C. E. Chase and R. Renard Tisza for suggesting this experiment, for playing an essential role in the ordering of the ammonium ion, for providing the encouragement and for continuing helpful advice and encouragement throughout the course of this work. Most of the crystallographic computations were carried out at the M.I.T. Computation Center.

Ultrasonic Investigation of the Order-Disorder Transition in Ammonium Chloride

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Introduction

The lambda transition in solid ammonium chloride was discovered by Simon [1] from heat-capacity measurements. An x-ray analysis by Simon and von Simson [2] showed that ammonium chloride has a CsCl-type cubic structure both above and below the critical temperature; thus the transition could not be due to a change in lattice type. Hetrich [3] found that ammonium chloride is weakly piezoelectric in the low-temperature modification, whereas it is not piezoelectric above the critical temperature. From this he concluded that the tetrahedral ammonium ions are oriented parallel in the low-temperature modification. Menzies and Mills [4] came to the same conclusion on the basis of the Raman effect. Paulling [5] suggested that the transition was related to the onset of free rotation of the ammonium ions, and quantitative refinements of this idea have been carried through by Fowler [6] and by Kirkwood [7]. In opposition to this, Frankel [8] interpreted the transition as being due to the order-disorder type, involving the relative orientations of the tetrahedral ammonium ions; it was assumed that in both the ordered and the disordered states the ammonium ions librate about an equilibrium position. This idea has been confirmed by many subsequent experiments.

In particular, Levy and Peterson [9] have carried out a neutron-diffraction determination of the hydrogen positions in both the low- and high-temperature modifications, and Purcell [10] has analyzed the neutron data to obtain the relaxation time for an NH4 ion to move from one orientation in its cubic cell to the other orientation. Both these investigations show that free rotation does not occur.

Indeed, in many respects NH4Cl is an ideal crystal for studying cooperative order-disorder phenomena. The ordering is completely analogous to that for a simple-cubic ferromagnet in a zero external field. The change in interaction energy between parallel and antiparallel NH4 ions is almost completely due to octopole-octopole terms, between nearest and next-nearest NH4 neighbors [11], and thus NH4Cl is quite a good example of an Ising lattice. Furthermore, the ordering process should have little effect on the dynamics of such an Ising lattice.

We wish to discuss here a variety of ultrasonic measurements which have been made on single-crystal ammonium chloride. Longitudinal and transverse (shear) acoustic velocities have been measured [12], [13] over a wide range of frequencies (5 to 60 Mc/s), temperatures (150 to 320 K) and pressures (0 to 12 kbar). The attenuation of longitudinal ultrasonic waves has been measured [14] at 1 atm for frequencies between 5 and 55 Mc/s and temperatures from 200 to 270 K. In all these investigations, special emphasis was given to the "anomalous" behavior near the lambda transition. As shown in Figure 1, the transition temperature is a fairly strong function of pressure, increasing from ~ 242 K at 1 atm to ~ 308 K at 10 kbar. (Note the pronounced curvature of the lambda line and the hysteresis observed at low pressures.) At a constant pressure of 1 atm, the ultrasonic velocities were originally measured by a pulse-echo method as a function of frequency and temperature, and no dispersion was observed [12]. Recently, the McSkimin pulse-superposition method has been used at a fixed frequency of 20 Mc/s. The temperature dependence at 1 atm has been restudied, and the pressure dependence of the velocities was measured at five fixed temperatures spaced between 250 and 300 K. Thus, we have very precise velocity data (~ 0.005%) on both the ordered and disordered phases. This experimental data will be described elsewhere [15] in detail, but is presented here in a graphical form.

Experimental Results

The variations of the shear constants c44 and c66 and of the compressional constant c11 with pressure at five different temperatures are given in Figures 2 and 3.
These constant-volume curves were obtained by determining the pressure required at a given temperature to give the desired volume (Bridgeman's data [15] and our own were used) and then reading the appropriate elastic constant values from figures 2 to 4.

For the shear constants, one can immediately see that most of the temperature change near \( T_1 \) and \( T_2 \) is due to the rapid change in volume in the transition region. Our data permit us to completely analyze the effects of volume changes and temperature changes so that one can see the effect of ordering at constant volume and temperature. For longitudinal waves, volume changes do have a significant effect on the velocity, but the anomalous dip in \( c_{44} \) is essentially due to ordering effects. In figure 7, the shift in the minimum between curves A and B is merely a result of the value chosen for the constant volume; the important difference between these curves is their shape near the minimum.

For shear waves there is no indication of excess ultrasonic attenuation near the lambda line, but for longitudinal waves there is a very sharp maximum in the attenuation coefficient \( \alpha \) at the transition point. Quantitative measurements of \( \alpha \) for longitudinal waves along [100] have been made at 1 atm as a function of frequency and temperature [14]. The results are shown in figure 8 for 15, 25, 45, and 55 Mc/s. Data have also been taken at 5 Mc/s, where a rather large (0.5 dB cm\(^{-1}\), temperature-independent background attenuation is present (presumably due to beam-spread losses).

Further experimental work on attenuation is currently in progress.

Since there is no excess attenuation near the lambda point for shear waves, it is possible to follow the behavior of the shear velocities through the transition region. Both \( c_{44} \) and \( C' \) showed a small hysteresis, the magnitude of which is indicated in the insert on figure 1. We have not shown data points in this region on figures 5 and 6 since equilibrium was very difficult to achieve (slow changes in the shear velocities occurred even after 45 min).

The presence of this hysteresis and the very abrupt change in shear velocities near \( T_1 \) are significant properties of our measurements at 1 atm. (Similar indications of hysteresis and abrupt changes near \( T_1 \) are seen from volume measurements and cooling curves.)

Discussion

Equilibrium data. Because of the formal analogy between the ordering of NH\(_4\)Cl and a ferromagnet in the absence of an external field, it is appropriate to consider the mechanical behavior of an Ising lattice. If the coupling between the lattice system and the "spin" system is sufficiently weak, an Ising lattice will become unstable in the immediate vicinity of its critical point and a first-order transition will occur. Furthermore, hysteresis will be expected in the critical region. This instability has been demonstrated for a two-dimensional square lattice [16, 17], where there is an analytic solution to the Ising problem. The important conditions for this instability are (1) weak lattice-spin coupling, (2) a finite compressibility for the disordered lattice, and (3) an infinite interaction energy. Such an instability has been proposed previously for other models [18, 19] and discussed in general thermodynamic terms by Rice [20], but little attention seems to have been paid to this problem. It would appear that NH\(_4\)Cl is a much more appropriate system for observing these effects than most ferromagnetic solids would be.

To illustrate the instability and the possible hysteresis in order-disorder transitions, let us look at the two-dimensional case [16]. Figure 9 shows a plot of \( \alpha \) and \(-\theta_0\) against the area \( \alpha \) at several temperatures \( T_1 < T_2 < \ldots < T_7 < T_8 \). The pressure
The change in area, $A$, and the free energy at point 5 on fig. 9) but as
for a system under zero external stress
isothermal compressibility
is the Ising heat capacity and internal energy at zero field as a function of $H = \frac{\Delta T}{T}$. The subscript $a$ denotes the appropriate quantity for a completely disordered lattice (for which $C_I$ and $C_{II}$ equal zero). The elastic constants $c_{II}$ are given by $(\partial^2 J/\partial\gamma^2)$, where the $\gamma$s are the appropriate strains. Thus the expression for $C_I$ will have a form similar to eq (2), and the dominant term in determining the shape of $C_I$ near $T_A$ will involve $C_I$. For $C = c_1c_1 - c_2c_2$ one requires a difference between two such expressions, and the singular part involving $C_I$ will cancel out.

The final expression for $C$ is complicated in its dependence on $V$ and $T$, but it does predict a smooth variation through the transition region. For $C_I$ the term containing $C_I$ disappears identically since $\partial^2 J/\partial \gamma^2 = 0$ (as the change in angle during a $\gamma$ shear, but $\partial^2 J/\partial \gamma^2 \neq 0$ and the shape of $C_I$ near $T_A$ is determined by $U_I$. In general terms these predictions are all fulfilled by our NH$_2$Cl data as functions of temperature at constant volume. In the case of $C_I$ one must take account of the significant difference between the adiabatic and the isothermal constants near $T_A$, but even so the shape of $C_I$ is strikingly related to the shape of the heat capacity curve. In addition, the shape of $C_I$ is what one would expect from an internal energy curve. No detailed discussion of $C$ will be given here, but it serves the purpose of showing that $C_I$ is very small for this shear mode and this indicates that the "anomalous" variations in $C_I$ and $C_{II}$ almost completely compensate each other.

A final remark about the equilibrium properties of NH$_2$Cl can be made in connection with the Pippard equations. It is known that these phenomenological relations are fairly well obeyed [12] in NH$_2$Cl, and a generalization of them in terms of stress-strain variables [22] shows that there are some unexplained difficulties. We have recently discussed the Pippard equations [23] on the basis of a three-dimensional Ising model and can now give a better insight into the reasons for their behavior.

\[ \frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_1} \]  

(4)

where $\tau$ is the relaxation time, $\tau_0$ is the relaxation time for the disordering of a disordered lattice point, $\tau_1$ is the relaxation time for the ordering of a disordered lattice point. These constants vary only slowly with temperature near $T_A$. We shall assume below that the quantity $\frac{1}{\tau_0} + \frac{1}{\tau_1}$ has a constant value (call it $B$) over the temperature range of

\[ B = \frac{1}{\tau_0} + \frac{1}{\tau_1} \]  

(3)

The phenomenological constants $A$ and $\delta$ depend on the substance involved but have a fixed ratio $A/\delta = 2$. A more general statistical-mechanical treatment of this problem has been given by Kikuchi [27]. For a temperature range $\delta$ close to the lambda point one can show that Kikuchi's results for the long-range relaxation times are still of the form given in eq (3). However, the constants $A$ and $\delta$ now depend on microscopic transition probabilities and the ratio $A/\delta$ near $T_A$ is $1.6$ rather than 2.

An essential feature of our ammonium chloride data which requires explanation is the fact that the attenuation $a$ has its maximum at $T_A$. One would expect $a$ to vanish at $T_A$ if it becomes infinite there. However, the theories mentioned above deal with $\tau_0$, the relaxation time for disordering at constant temperature and volume. The experimental conditions for measuring attenuation are adiabatic rather than isothermal, and although the process is isentropic the specific heat at constant volume is given in the form

\[ \frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_1} \]  

(4)

where $\dot{\kappa}$ is a rate constant, $C_I$ is the specific heat at infinite frequency (frozen) specific heat, and $\dot{\gamma}$ is a progress variable characterizing the internal (non-equilibrium) state of the system at a given $V$ and $T$.

The detailed behavior of $\partial J/\partial \gamma^2$ is not known, but it seems likely that this quantity varies only slowly with temperature near $T_A$. We shall assume below that the quantity $\dot{\kappa}(\partial J/\partial \gamma^2)$ has a constant value $(call \ it \ B)$ over the temperature range of
for the relaxation time associated with long-range order, where \( \Delta T = T - T_c \) and the constant \( A \) has different values above and below \( T_c \). According to eq. (5), \( a \) will have a finite maximum value at \( T_c \) and if this value is reasonably small (i.e., \( a \approx 1 \)) the attenuation will have its maximum at \( T_c \).

For a mechanism involving a single relaxation time, we have the usual expression

\[
\alpha \approx \frac{\epsilon - \epsilon_0}{2\epsilon_0} a \frac{\omega}{\omega_c} \left( \frac{\Delta T}{A} + 1 \right)^{-1},
\]

(6)

Unfortunately the variation of \( \epsilon(\omega) - \epsilon_0 \) with temperature is not known, but it is unlikely that this could be an important factor in determining the temperature of \( \alpha \). One would probably expect only a small and slowly varying temperature dependence of \( \epsilon(\omega) - \epsilon_0 \) on temperature. We shall assume (as did Chase in his analysis of helium [28]) that \( \epsilon(\omega) - \epsilon_0 \) has a constant value throughout the transition region. We shall also assume (and can subsequently justify) that \( a \approx 1 \) for all temperatures near \( T_c \). With these assumptions and eq. (5), we can rewrite eq. (6) in the form

\[
\alpha \approx 2 \frac{\epsilon - \epsilon_0}{\epsilon_0} \frac{\omega}{\omega_c} \left[ \frac{\Delta T}{2A} + \frac{1}{2} \right]^{-1}.
\]

(7)

If all our assumptions are valid, then \( a \approx 1 \) should be independent of frequency and should vary linearly with the temperature on both sides of \( T_c \).

Figure 10 shows a plot of \( \alpha(\omega) \) in units of \( \epsilon_c \) versus frequency for all of our data close to \( T_c \). Various details concerning the correctness for background attenuation and the justification of \( a \approx 1 \) are given elsewhere [14], but in general the way the data shown in figure 10 seem to agree with eq. (7). The value of \( a \approx 1 \) at its minimum (at ~242.0 \( K \)) is 0.52\% and the slope above \( T_c \) is 0.64 \( \times 10^6 \) and the slope below \( T_c \) is 0.46 \( \times 10^6 \). These slopes give a ratio \( A/\Delta T \approx 14.33 \), as compared to \( n = 1.6 \) expected on the basis of Kukush's model.

When the analysis is extended to data obtained at higher frequencies and at temperatures further away from \( T_c \), the deviations from eq. (7) are not

\[\text{Figure 10. Plot of } \alpha \text{ versus temperature, close to the lambda point in } g=1 \text{ state.} \]

\[\text{Data for } g=3 \text{ and } 4 \text{ are not available at the lower temperature range. Note that the curve in Figure 10 is a theoretical curve and subject to uncertainty.}

Discussion

E. R. Fisher: Let me try to summarize some experimental observations on the critical temperature and the critical point.

J. M. Rowland: I have a problem concerning the dimensions of the apparatus in which one tries to measure the transport properties at the critical point. As, for instance, one expects that any anomaly in viscosity or thermal conductivity is related to the long range correlations and fluctuations, one has to be taken into account the fact that the dimensions are large compared to the magnitude of the correlation length.

M. F. Fisher: It seems to me there is no need to worry about the dimensions relative to the correlation length because all our light scattering and neutron scattering experiments show that even when you have what you call long range correlations, they are still of the order of 100 \( A \) when you come very close to the critical point. And that is for the pair correlation function. Most of these transport coefficients involve higher order correlation functions which one would expect to die out more rapidly. This argument is perhaps valid. For instance, one would expect difficulties very close to the critical point. I don't think one has to worry about this in practice.

J. M. Rowland: In the case of a specular density of the reference point and the constant density, one has to consider the speculation between two finite values. This may suppress the explanation above given for the behavior of \( a \).

References