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Order-Disorder Transition in NH_4Cl. III. Specific Heat*

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The ac technique for measuring heat capacities is explained, and a model is presented to show the effects that the thermal properties of the heat link have on the observed temperature modulation. The ac technique is used to measure the heat capacity of ammonium chloride near the order-disorder transition at 242 °K. The measured heat capacities are analyzed using the theory presented in the first paper of this series. There is a strong sample dependence in the data that is not understood, but agreement with the theory is obtained for the sample with the sharpest transition. The critical exponents obtained from the fitting procedure are much closer to 1 than the theoretical values obtained from various model calculations.

I. INTRODUCTION

In a preceding paper[1] a theory to explain the behavior of a system that undergoes a second-order phase transition in a compressible lattice has been discussed. Ammonium chloride undergoes an order-disorder transition near 242 °K, and it has been suggested that it should behave like the Ising model in that region. In the following we shall describe a measurement of the heat capacity of ammonium chloride near the transition and use the theory presented in I to analyze the observed behavior. Comparisons will be made between our results and the behavior of the Ising model and also with the results of other experiments on ammonium chloride.

II. ac HEAT-CAPACITY TECHNIQUE

The heat capacity was measured by the ac technique that was introduced by Handler, Mapother, and Rayl[2] and by Sullivan and Seidel.[3] The technique involves the application of a time-varying heat to a sample that has loose thermal coupling to a temperature bath. It can be understood by examining the following example.

Consider a piece of material with heat capcity C and infinite thermal conductivity. Connect this material to a constant-temperature reservoir by means of a link with thermal resistance R. If the material is heated at a rate $Q = Q_0\, e^{i\omega t}$ and its temperature T is measured relative to the temperature of the reservoir, then T will change according to the relation

$$C\frac{\partial T}{\partial t} = Q_1 = Q - \frac{T}{R}\ .$$

Letting $T = T_1 e^{i\omega t}$, we find

$$T_1 = \frac{-iQ_0/\omega C}{1 - 1/i\omega RC} \simeq -\frac{iQ_0}{\omega C} \qquad (1)$$

if $RC \gg 1$. Thus, we have a simple relation between the temperature modulation of the material and its heat capacity.

In an actual experiment the relation between T_1 and C may be more complicated than Eq. (1) because of the finite thermal conductivity of the sample to be measured and the nonzero specific heat of the thermal link between the sample and the reservoir. We can find the effect of these parameters on the temperature modulation by solving the following problem.

Consider the one-dimensional system shown in Fig. 1. There are two pieces of material connected together. At $x = 0$, piece 1 is held at a temperature T_0 while at $x = l_2$, piece 2 is being heated at a rate $Q_0 e^{i\omega t}$. Each material has a specific heat c, a thermal conductivity κ, a density ρ, and an area A.

The temperature of the system is a function of x and t and is found by solving the heat-conduction equation

$$\frac{\partial T}{\partial t} = \eta_j \frac{\partial T^2}{\partial x^2}\ ,$$

where $j = 1, 2$ refers to the material and $\eta = \kappa/\rho c$ is the thermal diffusivity. The boundary conditions for the solution are that $T\,(x = 0) = T_0$ for all t and that the heat flow is continuous. Thus, we have

$$\kappa_2 A_2 \frac{\partial T}{\partial x}\bigg|_{x = l_1 + l_2} = Q_0 e^{i\omega t}\ ,$$

$$\kappa_2 A_2 \frac{\partial T}{\partial x}\bigg|_{x = l_{1+}} = \kappa_1 A_1 \frac{\partial T}{\partial x}\bigg|_{x = l_{1-}}\ .$$

The solution to this problem has the form $T(x, t)$

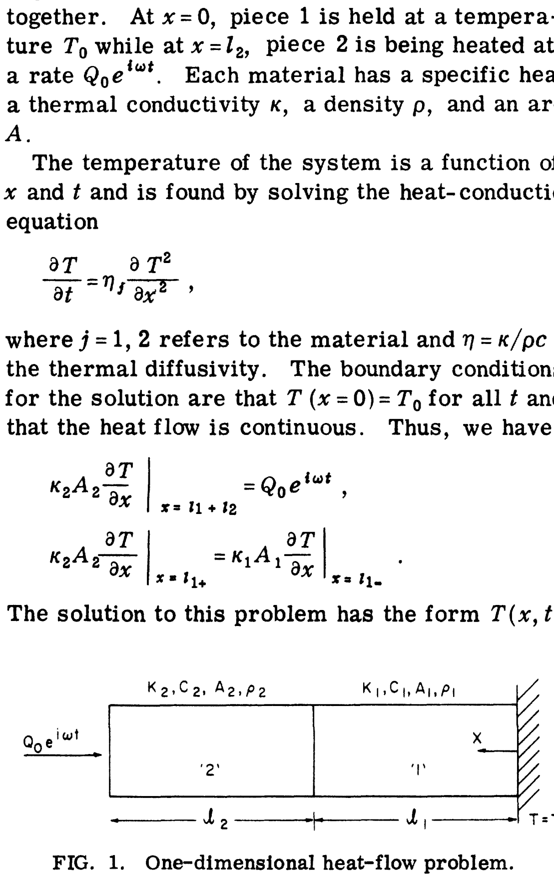

FIG. 1. One-dimensional heat-flow problem.

$= T(x)e^{i\omega t}$, where $T(x)$ is a complicated function[4] which simplifies at $x = l_1$ to

$$T(l_1) = \frac{iQ_0/\omega C_2}{(1/y_2)\sinh y_2 + (R_2/R_1)(y_1/y_2{}^2)\coth y_1 \cosh y_2}, \tag{2}$$

where

$$l_{0j} = \left(\frac{\eta_j}{\omega}\right)^{1/2}, \quad R_j = \frac{l_j}{\kappa_j A_j}, \quad L_j = \frac{l_{0j}}{i^{1/2}}, \quad y_j = \frac{l_j}{L_j}.$$

R is the thermal resistance of the material and l_0 is the characteristic thermal length. If we identify piece 2 with the sample whose heat capacity we are trying to measure, the requirement for uniform sample temperature is that $l_2/l_{02} \ll 1$. Expanding Eq. (2) we find

$$T(l_1) \simeq \frac{iQ_0/\omega C_2}{1 + (\tau_2/2\tau_1)(\frac{1}{5} + \tau_2/6!\tau_1)\omega^2\tau_2^2 + i[(1/3! + \tau_2/4!\tau_1)\omega\tau_2 - 1/\omega\tau_1]}, \tag{3}$$

where

$$\tau_1 = R_1 C_2 / y_1 \coth y_1, \quad \tau_2 = R_2 C_2.$$

It is clear that to recover the simple expression of Eq. (1), we want

$$|\omega\tau_1| \gg 1, \tag{4}$$

which is similar to the condition used to obtain Eq. (1). Then considering the magnitude of $T(l_1)$ we find

$$|T(l_1)| = T_{ac}\left(1 + \tfrac{2}{3}a_1\frac{\tau_2}{\tau_{dc}} + \frac{(\omega\tau_2)^2}{90} + \frac{a_1{}^2 + a_2{}^2}{(\omega\tau_{dc})^2} + \frac{2a_2}{\omega\tau_{dc}}\right)^{-1/2}, \tag{5}$$

where

$$\begin{aligned} T_{ac} &= Q_0/\omega C_2, \quad \tau_{dc} = R_1 C_2, \\ a_1 &= \frac{z}{2}\frac{\sinh z + \sin z}{\cosh z - \cos z}, \\ a_2 &= \frac{z}{2}\frac{\sinh z - \sin z}{\cosh z - \cos z}, \\ z &= (2)^{1/2} l_1/l_{01}. \end{aligned} \tag{6}$$

Equation (5) will allow us to determine what the parameters of the experiment should be in order for us to be able to use T_{ac} as a measure of the heat capacity of the sample without including any of the correction terms.

There are two limits where Eq. (5) is simple to analyze. When $l_1/l_{01} \ll 1$, $a_1 \simeq 1$ and $a_2 \simeq 0$, and the frequency-dependent corrections behave like $(\omega\tau_2)^2$ and $(\omega\tau_{dc})^{-2}$. However, when $l_1/l_{01} > 1$, $a_1 \simeq a_2 \simeq l_1/(2)^{1/2} l_{01}$, and the important frequency corrections behave like $(\omega\tau_2)^2$ and $(\omega\tau')^{-1/2}$ where $\tau' = R_1 C_2^2/C_1 = \tau_{dc} C_2/C_1$. It is important to note in this latter case that the effective low-frequency response time τ' contains a factor C_2^2 so that the correction term is independent of the sample heat capacity when multiplied by the C_2 in T_{ac}. We can see that it is better to work in the limit $l_1/l_{01} \ll 1$ since the corrections to the heat capacity will be less in this case.

Sullivan[5] has shown that attaching a thermometer and a heater to the samples introduces corrections to the ac temperature amplitude that are similar to those found in Eq. (5).

When all corrections are small, they will be additive. Thus, it will be easy to determine their relative importance either by calculation when the appropriate physical parameters have been measured or by a measurement of the frequency dependence of $T(l_1)$. We note that the size of the frequency-independent corrections lies between those of the high- and low-frequency corrections. Thus, if both the high- and low-frequency corrections are unimportant, the frequency-independent correction may be ignored.

III. EXPERIMENTAL METHOD

The most important considerations in designing the experiment were the temperature-stability requirements imposed by the desire to work at temperatures very close to the transition ($\Delta T/T \sim 10^{-5}$) and the time-constant requirements which resulted from the ac heat-capacity measurement. The temperature-stability requirements were met by doing the experiment in a copper container which was contained in a vacuum and whose temperature was controlled by automatically balancing an electrical heat leak against a cold leak from a liquid-nitrogen bath. The scheme for achieving the temperature control is shown in the top half of Fig. 2.

Because of the small thermal diffusivity of ammonium chloride, we were forced to go to low frequencies for the ac heat-capacity measurement. With a heating frequency of 0.033 Hz, ammonium chloride has a thermal length ~ 0.3 cm. Therefore use of a sample thickness of 0.3 mm was sufficient to ensure that there would be no significant correction to the observed temperature modulation even if the thermal diffusivity was ten times smaller at the transition. The other high-frequency cutoffs in the experiment were made high enough by mounting the thermometer, a 0.005-in.-diam thermistor, and the resistive heater on pieces of copper foil and attaching them to the sample with thin layers of silicone vacuum grease. The low-frequency requirements of the experiment were satisfied by using thin (0.0005-in.-diam) copper wire as one heat leak which was also the thermal link between the temperature-controlled container and the sample. The other electrical leads for the thermometer and heater were made with constantan wire and did not contribute significantly to the heat leaks.

The heat capacity of the sample assembly was measured by applying a triangular voltage to the resistive heater attached to the sample and measuring the ac component of the imbalance of the bridge circuit in the bottom half of Fig. 2. The resultant temperature modulation could be computed from the thermistor's temperature calibration curve. Then, Eq. (1) is used to find the heat capacity.

The ac signal was measured at room temperature as a function of heating frequency from 0.04 to 0.004 Hz in order to determine if the estimate of the low-frequency correction obtained from Eq. (5) was correct. The experimentally observed change of 5% in the signal was in reasonable agreement with the 2% change predicted from Eq. (5). Therefore, there were no low-frequency corrections to be made. High-frequency effects could not be measured because of the time constant used on the output of the lock-in, but they did not seem to be important since there was no noticeable phase shift of the ac signal as the sample went through the transition.

IV. SAMPLE PREPARATION

The samples for the experiment were single crystals grown by evaporation of solvent from a saturated solution of ammonium chloride in water with urea added in order to produce an acceptable growth habit. The ratio of urea to ammonium chloride was approximately 1 : 6. This procedure gives single crystals in the form of rectangular parallelepipeds which others[6] have reported as having no detectable amounts of urea incorporated in them. The size of the larger crystals was typically $\frac{1}{2}$ cm square and a few mm thick.

Because of the low thermal diffusivity of ammonium chloride, the crystals had to be made thinner in order to make the ac heat-capacity measurement practical. Two methods of thinning were used. For both methods the crystal was bonded to a holder with Apiezon W wax. Then the crystal was thinned either by rubbing over silicon carbide paper or over filter paper wet with distilled water. When the thinning was completed, the crystal was removed from the holder by dissolving the wax in toluene.

The sample thickness used was about 0.3 mm. This was thick enough not to break easily yet thin enough to make the high-frequency corrections in the heat-capacity measurement unimportant.

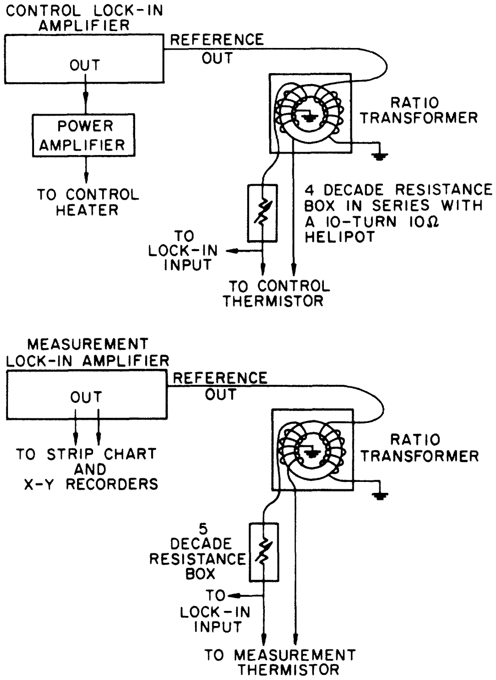

FIG. 2. Temperature measurement and control systems.

V. ANALYSIS OF HEAT CAPACITY

The specific heat as obtained from Eq. (1) is plotted in Figs. 3–5 for three different samples. The absolute magnitude of the specific heats was obtained by making the average experimental value between 246 and 248 °K agree with the value found by Extermann and Weigle[7] (1.46×10^7 ergs/g °K). The results shown are not inconsistent with the results of Voronel and Garber,[8] who measured C_p for ammonium chloride in order to determine the latent heat of the transition. Sample 2 was thinned by rubbing it over abrasive paper, and 5 was thinned by rubbing it over wet filter paper while 3 was a crystal that happened to grow with a reasonable surface area (~4×4 mm) and the appropriate thickness for the experiment.

Although data were taken on both sides of the transition on warming and cooling runs, only those points which precede the transitions are shown. The transitions occurred at 242.29 ± 0.01 °K on cooling and 242.59 ± 0.01 °K on warming. Beyond these temperatures Dinichert has mapped the surface of a crystal with x rays[9] and found that some of the crystal is in the ordered state and some in the disordered state. This heat-capacity measurement verified Dinichert's observation and also showed that there is a latent heat involved in the transformation. The evidence is given in Fig. 6, a strip-chart recording of the temperature of the sample as the transition is approached from high

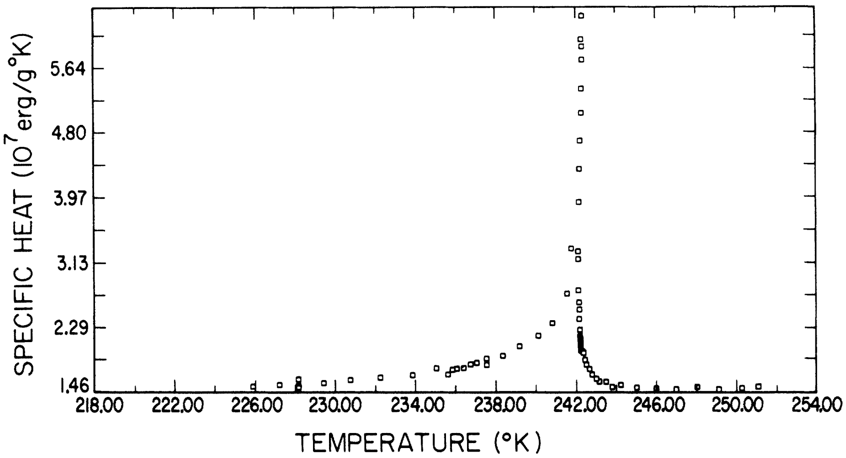

FIG. 3. Heat capacity of sample 2.

temperatures. Section 1 of the figure shows the sample relaxing to a new equilibrium temperature. The abrupt steps in this section correspond to adjustments made in the bridge circuit to achieve balance, which is at 50 on the chart. In section 2 we start to cool the sample toward a lower equilibrium value. The breaks in this part do not correlate with any external disturbances. We believe they are places at which a portion of the sample transforms from the disordered to the ordered state giving up some latent heat which then raises the temperature of the sample package. Note that the amplitude of the temperature modulation at the end of section 2 is much smaller than it was before the transition started. This corresponds to the larger heat capacity of the ordered state which is evident in Figs. 3–5.

Similar behavior is observed when the transition is approached from low temperatures. In this case a part of the crystal going from the ordered to the disordered state absorbs latent heat and lowers the temperature of the sample package. We have excluded data from the mixed-phase regions since the theoretical results are all for single-phase systems.

The experimental results were compared to the theory by constructing the function

$$\chi^2=\sum_i \left[(C(T_i)-C_i)/C_i\right]^2 ,$$

where the summation is over all experimental points, C_i is the measured heat capacity at the temperature T_i,

$$C(T)=C_{V_0}+(a/T_0)(2-\alpha)(1-\alpha)|\epsilon|^{-\alpha}$$
$$+\left[\frac{a(2-\alpha)(1-\alpha)|\epsilon|^{-\alpha}}{V_0}+\frac{n\beta_0 T_0}{n^2\kappa_{T_0}}\right]$$
$$\times\left[\frac{n\beta_0 V_0+(an^2\kappa_{T_0}/T_0)(2-\alpha)(1-\alpha)|\epsilon|^{-\alpha}}{1-(a/V_0)n^2\kappa_{T_0}(2-\alpha)(1-\alpha)|\epsilon|^{-\alpha}}\right], \quad (7)$$

and ϵ is found from

$$0=-D'(a/V_0)n^2\kappa_{T_0}(2-\alpha)|\epsilon|^{1-\alpha}$$
$$+\epsilon-(\Delta T/T_0)+n\beta_0\Delta T . \quad (8)$$

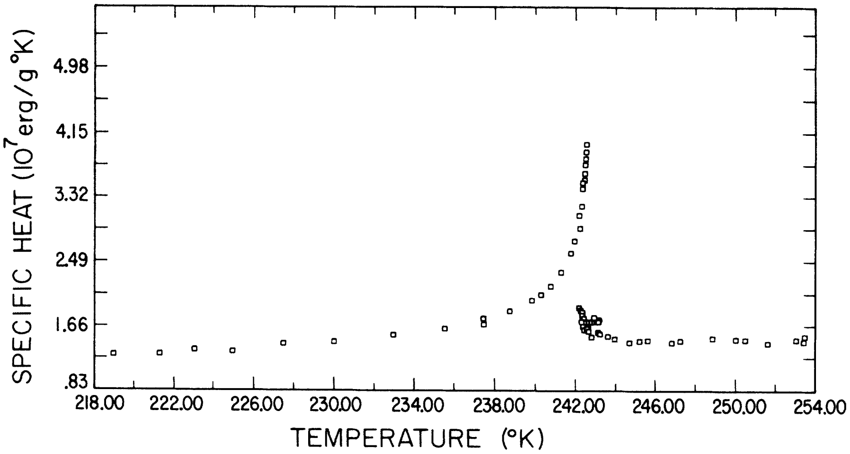

FIG. 4. Heat capacity of sample 3.

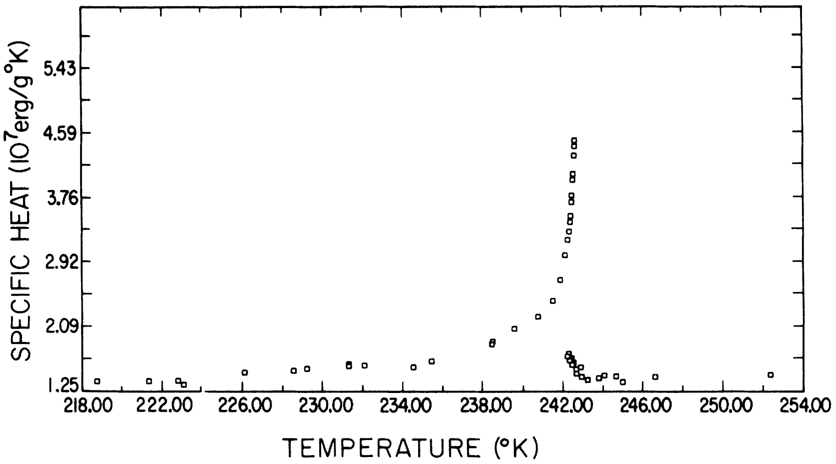

FIG. 5. Heat capacity of sample 5.

Equations (7) and (8) come from Eqs. (7), (8), and (10) in I with p and p_2 set equal to zero. We note that ΔV has been eliminated from Eqs. (7) and (8) and that n, κ_{T_0}, and β_0 are not completely determined by the heat-capacity measurement since they only appear in the quantities $n^2\kappa_{T_0}$ and $n\beta_0$. In order to find values for n and the nonsingular parts of the compressibility and thermal expansion, some assumption must be made about the behavior of the volume. This may be done by choosing one of the constants to agree with another measurement of that constant or by choosing the constants so that the theoretical ΔV-ΔT curve given by Eq. (8) matches some feature of a measured ΔV-ΔT curve, e.g., the volume discontinuity at the transition.

The latter alternative is difficult to use since it is hard to determine where the transition is on the almost vertical portion of the ΔV-ΔT curve. Both methods are complicated by the facts that the fits were not very sensitive to the value of β_0 and that the values reported for the background thermal expansion above the transition[9–13] vary from about $1.5\times 10^{-4}\,°\mathrm{K}^{-1}$ to $6\times 10^{-4}\,°\mathrm{K}^{-1}$. The function χ^2 was minimized by using a large digital computer to vary the parameters in Eq. (7). The variation was controlled by a program that utilized Rosenbrock's rotating-coordinate-system method to find local minima of χ^2.

Most of the computation was done using the data from sample 2. The best fits found had $\chi^2 \simeq 2.8\times 10^{-4}$ which is what is expected for a good fit with experimental errors ~ 1–2% and are shown in Figs. 7–10. Table I contains a typical set of parameters. Other equally good fits were found with values of the parameters which varied 30% from those in Table I, except for the values of $n\beta_0$ which could be

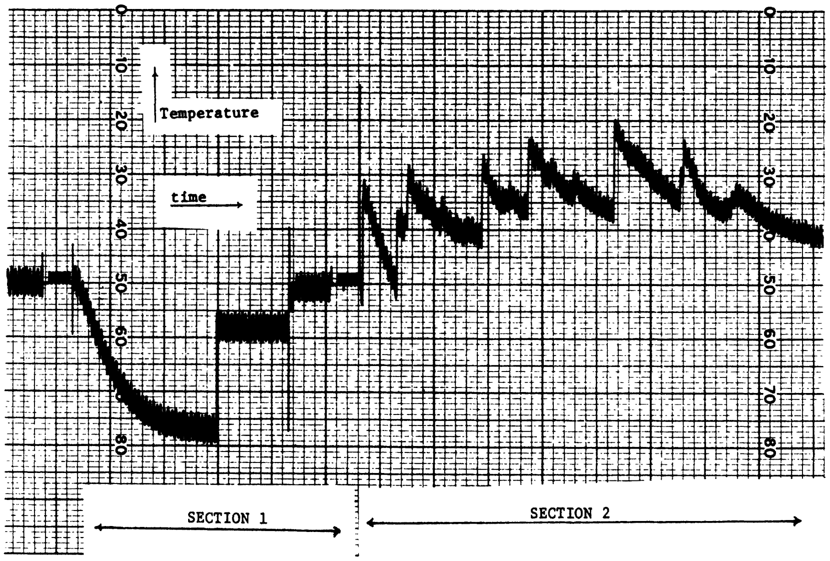

FIG. 6. Temperature of a sample going through the transition.

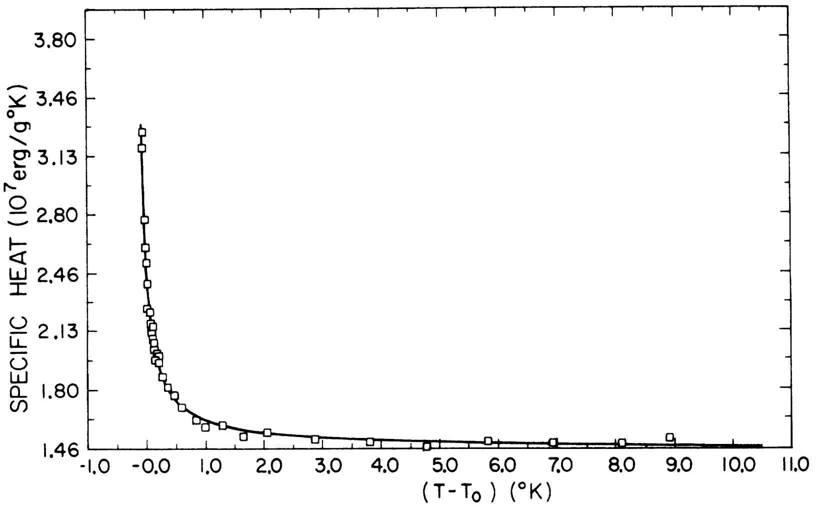

FIG. 7. Theoretical fit to the heat capacity of sample 2 above the transition.

changed by an order of magnitude and of $n^2\kappa_{T_0}$ which could be changed by a factor of 2 or 3.

We can see from Fig. 3 that the heat capacity at the transition is finite. Constraining the theoretical curve to go through the experimental points must put the infinity in C_p, which is predicted by Eq. (7) at the transition, at a temperature different from the observed transition temperature. Therefore, we expect that the hysteresis predicted by the parameters in Table I will be larger than the observed hysteresis. In fact, the predicted hysteresis turns out to be about 0.43°K which is about 50% larger than is observed.

If we force the volume discontinuity to agree with that found experimentally,[10] the numbers in Table I give n, β_0, and κ_{T_0} as 1.3, 3.8×10^{-4} °K^{-1}, and 5.9×10^{-11} (cgs). The value of β_0 is within the range of values reported in the literature for the background thermal expansion $[(1.5-6)\times10^{-4}$ °$K^{-1}]$.

Garland and Renard[14] have obtained a value of 5.9×10^{-12} (cgs) for the disordered lattice compressibility by extrapolating the temperature and pressure dependence of the compressibility to the transition region, and Bridgman[15] has obtained that number for the compressibility at 273 °K. Using this value for κ_{T_0}, the numbers of Table I give $n\simeq4$ and $\beta_0=1.2\times10^{-4}$ °K^{-1} and the predicted volume discontinuity is three times smaller than that found by Fredericks.[10]

Garland and Renard[14] have derived the slope of the line of transitions in the V-T plane from their compressibility experiments. They denote this quantity by $(1/V_\lambda)(dV/dT)_\lambda$ and find a value of -4.17×10^{-4} °K^{-1} for it. This quantity can also be obtained from Bridgman's[15] measurement of the volume as a function of pressure at 273 and 303 °K. His results indicate a value of -7.3×10^{-4} °K^{-1}. We can try to interpret $(1/V_\lambda)(dV/dT)_\lambda$ by noting that Eq.

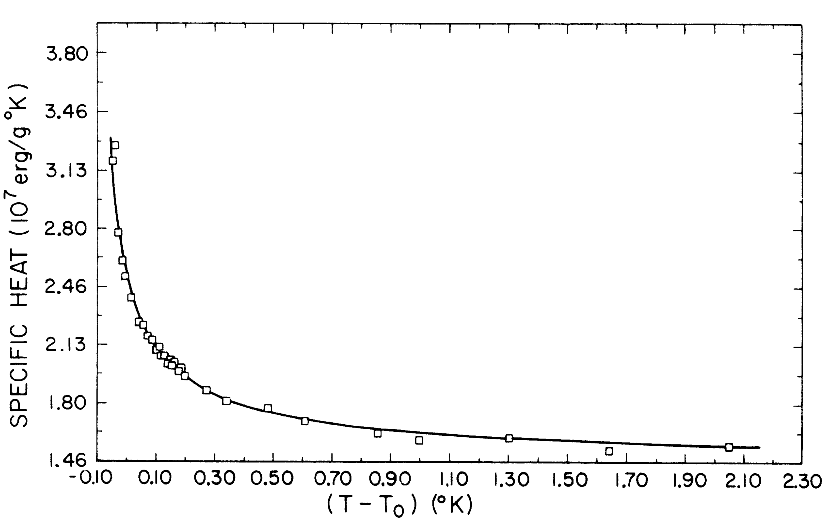

FIG. 8. Theoretical fit to the heat capacity of sample 2 above the transition; temperature scale expanded.

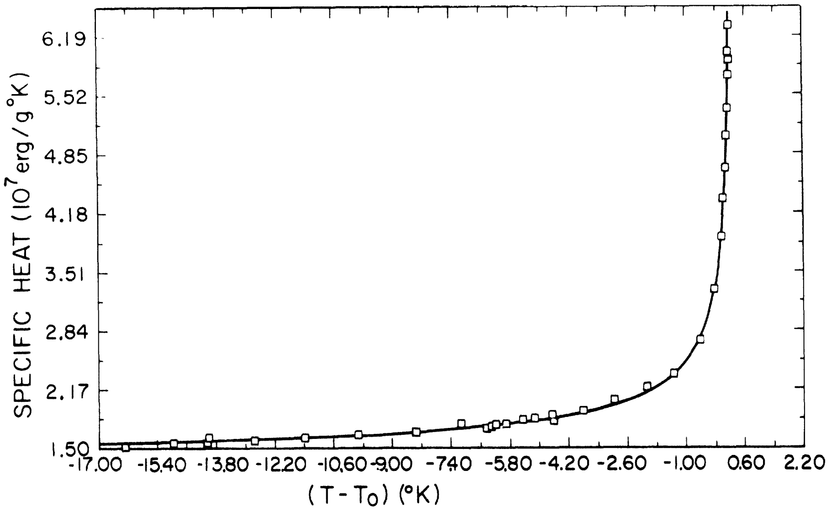

FIG. 9. Theoretical fit to the heat capacity of sample 2 below the transition.

(8) in I predicts that the transition will occur when

$$|\epsilon|^{\alpha}=|\epsilon_{tr}|^{\alpha}\equiv an^{2}\kappa_{T_0}(2-\alpha)(1-\alpha)/V_0\ . \tag{9}$$

Then Eq. (5) in I gives us

$$\frac{(\Delta V)_{tr}}{V_0}=\frac{1}{n}\left(\epsilon_{tr}-\frac{(\Delta T)_{tr}}{T_0}\right) \tag{10}$$

so

$$\frac{1}{V_\lambda}\left(\frac{dV}{dT}\right)_\lambda=\frac{1}{V_0}\frac{d(\Delta V)_{tr}}{d(\Delta T)_{tr}}=-\frac{1}{nT_0}\ . \tag{11}$$

This result applied to Garland and Renard's and Bridgman's findings gives $n=9.9$ and 5.7, respectively. These values are somewhat larger than the results of the fitting procedure. However, there is some reason to doubt whether the numbers from the pressure experiments should be compared with the numbers found in this paper. This uncertainty arises because Garland and Renard report that the temperature hysteresis of the transition disappears as the pressure is raised while, as we show below, the approach that we use predicts that the temperature hysteresis is independent of pressure.

From Eq. (7) in I we find the values of the transition temperatures upon cooling and heating using the appropriate ± subscripts in each case:

$$(\Delta T)_{tr}=\frac{p-p_0+(\alpha/V_0)n\ (2-\alpha)\,|\epsilon_{tr}|^{1-\alpha}+\epsilon_{tr}/n\kappa_{T_0}}{(\beta_0+1/nT_0)/\kappa_{T_0}}\ . \tag{12}$$

Since ϵ_{tr} [see Eq. (9)] does not contain the pressure, the coefficient of p in Eq. (12) does not depend upon the direction from which the transition is approached. Therefore, the predicted hysteresis will be independent of the pressure. This result indicates that the small-argument expansions

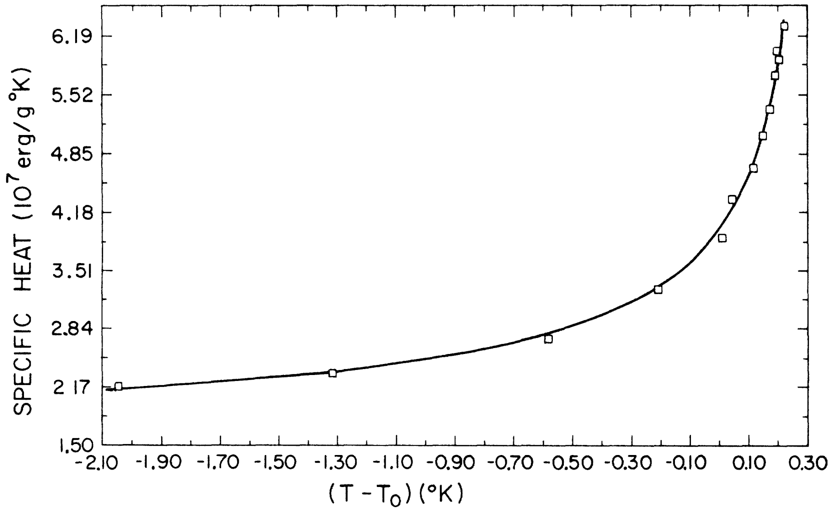

FIG. 10. Theoretical fit to the heat capacity of sample 2 below the transition; temperature scale expanded.

used in this paper are not valid in the region of Garland's measurements.

The parameters α_+ and α_- are of particular interest in connection with the underlying second-order nature of the transition. The large values found for α_+ and α_-, ~0.8 and ~0.7, respectively, are very different from those calculated by Wakefield[16] for the simple-cubic Ising model. In the range of $|\epsilon|$ available to the experiment, greater than 5×10^{-4} as estimated from the fits, the calculations predict a value for α less than $\frac{1}{8}$. If the fitting procedure is changed by not including the data near the transition, then it becomes possible to obtain fits with a wide range of α's, including small ones. However, the large α's found for the best fits to sample 2 are in qualitative agreement with the results of the volume-versus-temperature measurements by Fredericks.[10]

No extensive fitting program was carried out for the data from samples 3 and 5. The loss of the heat-capacity peak on the high-temperature side for these samples removed some of the information content of the curves and made it possible to obtain fits with wider ranges of parameters. Also, it is well known that most second-order phase transitions exhibit deviations from the theory called rounding which tend to limit the height of the heat-capacity peak and broaden it out. Even if this type of rounding was not present it is difficult to imagine a situation where the observed heat capacity would be larger than the ideal system at the transition. Therefore, we chose the largest, sharpest peak to compare with the theory.

VI. CONCLUSIONS

The differences observed in the behavior of the samples are quite interesting. Most striking are the differences in the values of the specific-heat peaks on the cooling curve. Figures 3–5 show that this peak was 5–6 times smaller for samples 3 and 5 than it was for 2. On the heating curve where the differences are not as extreme the specific-heat peak for 3 was only slightly more than $\frac{1}{2}$ that for 2 while 5 was about 15% larger than 3.

We note that there is a consistent trend in the behavior of the samples. Sample 2 has the largest, sharpest heat-capacity peaks while sample 3 has the smallest, broadest peaks. This behavior correlates with the way the samples were thinned for the measurement. Sample 2 was sanded, 5 was chemically etched, and 3 was not thinned at all. Thus, the rougher the treatment during thinning, the larger and narrower is the heat-capacity peak.

When dealing with second-order transitions we usually expect some factor such as temperature inhomogeneities, impurity content, or crystal imperfections to limit the singularities predicted by the theory at some small value of $|\epsilon|$.[17] Thus, we might suppose that the peaks displayed in Fig. 3 are depressed due to some factor, such as there being a distribution of transition temperatures in the samples. However, we would then expect that a more perfect crystal would have a larger anomaly in the heat capacity. The trend we observe above goes in the opposite direction. The sample receiving the roughest thinning had the sharpest peak. Further evidence for this trend was obtained by annealing sample 2 and then remeasuring the heat-capacity peaks. After annealing the sample at 100 °C in a dry nitrogen atmosphere for $\frac{1}{2}$ day, the peak height on the warming curve was about a factor of 2 smaller, and the cooling curve was qualitatively much like those of sample 3 and 5. We cannot try to explain this behavior since there were not sufficient data to determine what physical factors are controlling the critical behavior. However, we feel that it could be caused by the fact that the measurement is only sampling part of the heat capacity of the Ising system and that the presence of lattice defects might increase the coupling to the Ising system thereby increasing the amount of the Ising heat capacity that is sampled.

The qualitative agreement of most of the parameters obtained from the fits with those obtained from other experiments is a sign that the theory presented in I is capable of representing the behavior of ammonium chloride. While there is some inconsistency between the characteristics of the theoretical model found from fitting the specific-heat data and the experimental characteristics of ammonium chloride found in the literature, this should not be taken as proof that the model is not applicable. There are two reasons for this conclusion. The principal one is the considerable variation in the reported characteristics of ammonium chloride when the same parameter has been measured by

TABLE I. Typical fitting parameters for sample 2.

Parameter	Value
V_0	$7.74\times10^{-3}\,cm^3$
T_0	242.164 °K
α_+	0.826
α_-	0.673
a_+/V_0	$7.42\times10^{4\,a}$
	2.39×10^{7} (cgs)
a_-/V_0	$5.78\times10^{5\,a}$
	1.86×10^{8} (cgs)
$n\beta_0$	4.83×10^{-4} °K^{-1}
$n^2\kappa_{T_0}$	$3.88\times10^{-8\,a}$
	9.56×10^{-11} (cgs)
$C_{V_0^+}/V_0T_0$	219^{a}
	7.05×10^{3} (cgs)
$C_{V_0^-}/V_0T_0$	206^{a}
	6.63×10^{3} (cgs)

[a] Experimental values expressed in arbitary units.

more than one investigator. This phenomenon is particularly evident in the results reported for the background lattice thermal expansion and the size of the volume discontinuity at the transitions. It even shows up in the value of the molar volume at the transition where there appears to be a spread of ~1% in numbers that are reported to five significant figures.[9,11,13,14] The other reason is that since it is evident that the specific heat does not uniquely determine the set of parameters in the theory, it is quite possible that further computer searches would uncover other sets of values for the parameters which would fit the specific heat and also provide better quantitative agreement with other properties. However, further analysis is not warranted because of the uncertainties connected with existing data.

The larger values found for α are definitely not in accord with most calculations of critical behavior. Recent experiments performed by Ashman and Handler[18] on β brass near its order-disorder transition which remains second order have shown agreement with Ising-model calculations. We do not know whether the disagreement found for the ammonium chloride system indicates that the model presented in I is too simplified to represent ammonium chloride well (for example, the fluctuations in volume are neglected), or represents the fact that we still have substantial structure-sensitive effects in our best sample.

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