

Heat capacity of NH_4Cl and ND_4Cl single crystals at high pressure *

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The constant-pressure heat capacity of NH_4Cl and ND_4Cl has been investigated in the vicinity of the order-disorder transition at 1 atm and at high pressures. The ac calorimetry technique has been used and has been shown to work well for investigating solid samples under hydrostatic gas pressures up to ~ 3 kbar. The "multicritical" pressure (above which the transition is continuous and below which a small first-order instability occurs) is 1500 bar for NH_4Cl and is very close to 1 atm for ND_4Cl . A correspondence was found between the C_p variation for ND_4Cl at 1 atm and NH_4Cl at 1500 bar and also between that for ND_4Cl at 1500 bar and NH_4Cl at 3134 bar. At the multicritical pressure, the behavior of the heat capacity in the ordered phase can be well represented by a power law, and the critical exponent $\alpha' = 0.50 \pm 0.07$ for ND_4Cl and 0.57 ± 0.07 for NH_4Cl . At higher pressures, the peak C_p values are significantly but reversibly decreased and the data show systematic deviations from a single power-law fit.

I. INTRODUCTION

Ammonium chloride crystals undergo an order-disorder transition involving the relative orientations of the NH_4^+ ions. At room temperature these ions are distributed at random with respect to two equivalent orientations, while below the transition they are parallel to each other ("ferro-ordered"). This system is of special interest because a small discontinuous phase change is observed at low pressures, but the transition becomes continuous above 1500 bar.¹ Thus there is a high-pressure "multicritical" point in NH_4Cl . Furthermore, the first-order aspect of the transition is very sensitive to deuteration, and the multicritical point in ND_4Cl lies close to 1 atm.² The detailed nature of this multicritical point is not yet understood. Although formally similar to the tricritical point observed in metamagnets and ^3He - ^4He , the available critical exponents do not correspond to those of a Gaussian tricritical point. Further details are given in Refs. 1 and 2 and the references cited therein.

Measurements of the heat capacity represent a well-established method of studying order-disorder transitions, and a variety of thermal measurements have been made previously on the ammonium chlorides. In particular, there have been extensive investigations of the heat capacity of NH_4Cl at 1 atm. Stephenson,³ Chihara and Nakamura,⁴ and very recently Amitin *et al.*⁵ have all made adiabatic calorimetry measurements on powdered samples from 20 to 300 K; and these data are in good agreement with each other. Thermograms obtained in the transition region by Voronel and Garber⁶ provide details about the hysteresis associated with the 1-atm transition, as does the ac calorimetry study of single-crystal samples by Schwartz.⁷ In

the latter investigation, high-resolution heat-capacity data were obtained approaching the transition both on warming and on cooling, and a hysteresis of 0.3 K was observed in the first-order transition temperature. Analyses of heat-capacity data in terms of critical exponents have been reported by Schwartz⁷ and by Amitin *et al.*,⁵ but in both cases these attempts are complicated by the substantial first-order character of the transition at 1 atm. Previous efforts to investigate the heat capacity of NH_4Cl at high pressures⁸⁻¹⁰ have not provided reliable quantitative data. In the case of ND_4Cl , there has been very little previous work on heat capacities. There are unpublished adiabatic calorimetry measurements by Stephenson³ on powdered ND_4Cl samples from 20 to 300 K at 1 atm, and there are differential thermal analysis measurements by Trappeniers and van der Molen,¹⁰ who carried out 1-atm and high-pressure studies of both NH_4Cl and ND_4Cl .

The present investigation involves measurements of the isobaric heat-capacity variation for both NH_4Cl and ND_4Cl single crystals at 1 atm and at high pressures. The resulting data are analyzed to obtain critical exponents α' near the multicritical point. The value of this critical exponent, which cannot be obtained from the previous thermal studies cited above, will help to establish the character of this special point at which the transition changes from first order to continuous. A brief account of the experimental method, which involves an adaptation of the ac calorimetry technique for use at hydrostatic gas pressures up to ~ 3 kbar, is given in Sec. II. The heat-capacity variations for several samples at 1 atm, 1500 bar, and 3134 bar are presented in Sec. III. The analysis of these data in terms of critical exponents and a general discussion of the results are presented in Sec. IV.

II. EXPERIMENTAL METHOD

The ac calorimetry technique, which is ideally suited to the study of the large heat-capacity peaks occurring at order-disorder phase transitions, can fortunately be utilized quite well at high gas pressures. There are several physical design limitations (especially the use of thin samples and low frequencies) that must be considered, and the theory of the method must be extended to take into account high gas densities and low sample thermal conductivities. A complete description of the theory, design, and testing of high-pressure ac calorimetry has been given elsewhere,¹¹ and only the essential features will be summarized here.

The sample was a thin slab of uniform thickness and cross-sectional area A . One face was coated with a very thin epoxy resistance heater, and a VECO-31A401A microbead thermistor was cemented to the center of the opposite face. The sample with attached addenda was suspended by very thin heater leads in the gas pressure vessel. The heat input due to an applied ac voltage of frequency f is $\dot{Q} = \dot{Q}_0(1 + \sin\omega t)$, where $\omega = 2\pi(2f)$. As a result of this heat input, the temperature of the thermistor undergoes a small oscillation with a peak-to-peak temperature amplitude ΔT_{ac} . The relationship between the experimentally determined quantity $(2\dot{Q}_0/\omega\Delta T_{ac})$ and the heat capacity per unit cross-sectional area (C_p/A) for a slab of thickness l_2 can be written in the form [see Eq. (21) of Ref. 11]

$$\frac{\gamma^2 \left(\frac{2\dot{Q}_0}{\omega\Delta T_{ac}} \right)^2}{A^2} = D \left(\frac{C_p}{A} \right)^2 + 2\delta_{eff} \left[B \left(\frac{C_p}{A} \right) + E\delta_{eff} \right]. \quad (1)$$

The quantity γ is a dimensionless and temperature-independent calibration factor corresponding to the ratio of the actual input heat flux at the center of the face to the ideal value \dot{Q}_0/A that would pertain if the heating were completely uniform. The coefficients B , D , and E are functions of $\omega\gamma\delta$, where $\delta = (2\rho_1\bar{C}_1\lambda_1/\omega)^{1/2}$ is determined by the gas properties and $\gamma = 2l_2/3\lambda_2$ is determined only by the sample properties. At 1 atm ρ_1 is very small, which leads to $\delta \approx 0$ and $B = D = E = 1$. At high pressures, these coefficients are greater than unity and are weakly frequency and pressure dependent. Finally, $\delta_{eff} = \delta(A_{eff}/A)$, where the ratio A_{eff}/A is a geometric factor with the constant value 1.25 for the configuration used in this experiment.¹¹ All the results reported here were obtained at the fixed frequency $\omega = 0.41$ (i.e., $f = 0.0325$ Hz), at which Eq. (1) has been tested and shown to be a valid expression over a wide range of pressures.¹¹ Note also that at 1 atm the right-hand side of Eq. (1) simplifies to $(C_p/A)^2$ and one obtains

$$C_p = r(2\dot{Q}_0/\omega\Delta T_{ac}), \quad (2)$$

in agreement with the ac calorimetry expression usually used at 1 atm.

Uncertainties in the experimental quantity $(2\dot{Q}_0/\omega\Delta T_{ac})$ were due primarily to random errors in the measurements of \dot{Q}_0 and ΔT_{ac} . The frequency ω , which was determined for each datum point by measuring the average period over ten cycles, made a negligible ($\pm 10^{-4}\%$) contribution to the uncertainty. Digital multimeter values of \dot{Q}_0 were accurate to within $\pm 0.2\%$. The oscillating temperature amplitude ΔT_{ac} was measured by averaging over 20 cycles the output of the lock-in amplifier displayed on a chart recorder, and the resulting uncertainty was $(0.5-1)\%$ over a wide range of amplitudes.

The large single crystals of NH_4Cl and ND_4Cl (99.2% deuteration) used in this investigation were the same as those used previously for piezoelectric measurements.² Thin slabs, cut parallel to one of the well-developed (100) faces by using a diamond saw, had dimensions of approximately $1 \times 1 \times 0.05$ cm and weighed about 60 mg. These samples had no visible defects in the interior, but striations caused by the diamond saw could be seen on the surface. Care was taken to minimize exposure to moisture in the air, and the samples were stored in a vacuum desiccator when not mounted in the calorimeter.

Measurements made in the high-pressure cell¹¹ were carried out over the range 240–300 K, and the bath temperature could be held constant to within ± 5 mK over a period of 5 h. For measurements at 1 atm, a separate calorimeter somewhat similar to that described by Schwartz⁷ was used over the range 200–300 K. Both warming and cooling runs were made at 1 atm (i.e., data points were taken at "bath" temperatures which were progressively increased or decreased). Only warming runs were carried out at high pressures, since the pressure could then be maintained at a constant value (± 2 bar) by venting small amounts of gas through a needle valve.

In the ac calorimetry method, the time-averaged sample temperature is greater than the "bath" temperature by an amount ΔT_{dc} .¹¹ This dc offset is typically 30 mK at 1 atm, but varies with the gas pressure and, to a lesser extent, the temperature. Thus, it is preferable to determine temperatures with the thermistor attached directly to the sample rather than a thermocouple mounted in the outer wall of the pressure vessel. Unfortunately, it was found that the thermistor calibration shifted with changes in the pressure. However, the sensitivity was essentially constant and this shift could be handled by merely changing the R_0 value. At a given pressure, the absolute temperature of the transition was taken from previous determina-

tions^{2-10, 12-14} and the R_0 value was adjusted so that the heat-capacity peak occurs at this temperature. Since we are primarily interested in determining changes in temperature in order to obtain values of the reduced temperature $t = |T - T_c|/T_c$, this necessity for recalibration is not a serious disadvantage. It should be noted that sample equilibration time was allowed at each temperature before a measurement of ΔT_{ac} was made. Indeed close to the transition the sample was equilibrated for ~2 h at each point.

III. RESULTS

Before presenting the experimental results, it is necessary to describe how the calibration factor r and the heat capacity of the addenda (heater, heater leads, and thermistor) were handled. Absolute values of the heat capacities of ammonium chlorides were obtained by normalizing our data to previously measured 1-atm C_p values at 280 K. This reference temperature, chosen to be far enough above the transition so that critical contributions to C_p would be negligible, lies in a region where C_p shows a slow linear variation with temperature. As can be seen from Eq. (2), remembering that C_p in Eqs. (1) and (2) represents the total heat capacity $C_p(\text{NH}_4\text{Cl}) + C_p(\text{addenda})$, the values of r and $C_p(\text{addenda})$ are interrelated. For all samples (and all pressures), we have assigned $C_p(\text{addenda})$ the constant value 0.01275 J K^{-1} on the basis of a calculation involving the composition and weight of the various addenda components. Using this value, one then finds 1-atm r values close to the ideal value of 1: $r = 1.00$ for ND₄Cl sample A, $r = 1.217$ for ND₄Cl sample B, and $r = 1.074$ for NH₄Cl sample B. As an indication of the magnitude of possible systematic errors in $C_p(\text{NH}_4\text{Cl})$, let us assume that the value of $C_p(\text{addenda})$ should be 0.015 J K^{-1} . This would lead to an increase of ~3% in the value of r . Since r is a multiplicative factor in Eq. (1), a change in this parameter will not influence the critical exponents obtained from the data.

In order to use Eq. (1) for the reduction of high-pressure data γ and A_{eff}/A must be specified in addition to r and $C_p(\text{addenda})$. We have used the value $\gamma = 1.91 \text{ J}^{-1} \text{ K cm}^2 \text{ sec}$, based on the known thermal conductivity of NH₄Cl at 1 atm and 280 K,¹⁵ and have found that this value and the ratio $A_{\text{eff}}/A = 1.25$ are consistent with our data over a wide range of pressure (see Ref. 11). In the analysis of data obtained at 1500 and 3134 bar, γ was taken to be independent of temperature and pressure although the thermal conductivity data¹⁵ at 1 atm indicate that γ should change from about 1.7 to 2.1 $\text{J}^{-1} \text{ K cm}^2 \text{ sec}$ throughout the temperature range of

our measurements. This neglected variation would introduce a systematic change of only $\pm 0.5\%$ in the final C_p values since γ plays a very minor role in the analysis. Fortunately, the dominant correction involved quantity in the reduction of high-pressure data with Eq. (1) is δ , which depends only on ω and the well-known properties of argon gas (see Ref. 11 for citation of appropriate references to Michels and co-workers).

In order to determine the value of r at high pressures, it was assumed that the high-pressure heat capacity at 280 K was equal to the 1-atm value. It follows from the relation $(\partial C_p / \partial p)_T = -T(\partial^2 V / \partial T^2)_p$ and the known temperature variation of the 1-atm thermal expansion coefficient¹⁶ that $(\partial C_p / \partial p)_T = -7.0 \times 10^{-4} \text{ J K}^{-1} \text{ mol}^{-1} \text{ bar}^{-1}$ for NH₄Cl at 280 K. This means that C_p increases by only 0.86% per kbar (assuming C_p is linear in p over the entire range). Since the corrections that have to be applied at 1500 bar amount to about to 40% of the sample heat capacity and these corrections are responsible for uncertainties of ~3% in C_p , we cannot achieve absolute accuracies of 1%. Therefore, for simplicity, the predicted small variation in C_p has been neglected. The r values resulting from this assumption are satisfyingly close to their 1-atm values: $r = 0.979$ for ND₄Cl sample A at 1500 bar and $r = 1.207$ for ND₄Cl sample B at 1500 bar.

NH₄Cl results. Two warming and two cooling runs were made on single-crystal NH₄Cl (sample B) over the range 200–300 K at 1 atm. All four runs were in excellent agreement throughout this range except for the expected systematic differences between warming and cooling data in the immediate vicinity of the transition. (There is a hysteresis of 0.4 K in the temperature of the heat-capacity peak on warming and cooling.) Some of our data in the 230–255 K region are shown in Fig. 1. Also displayed are adiabatic calorimeter data on a powdered sample reported by Amitin *et al.*⁵ The calibration factor $r = 1.074$ was chosen to achieve agreement between our C_p value at 280 K and the value $C_p = 82.0 \text{ J K}^{-1} \text{ mol}^{-1}$ obtained from Amitin *et al.* With this choice of r , there is good agreement between the two sets of data over the range 260–300 K (differences less than 1.5% and random), but the C_p values of Amitin *et al.* lie systematically (~3%) above our values between 244 and 255 K. In the immediate region of the transition, meaningful comparisons are difficult since the adiabatic calorimetry C_p values are artificially high due to smeared-out latent heat effects. However, it is obvious from Fig. 1 that the present C_p values are smaller than the adiabatic calorimeter values in the 235–242 K range. Furthermore, our ac calorimeter values are slightly larger than those reported by Amitin *et al.* in the 200–225 K range. Thus,

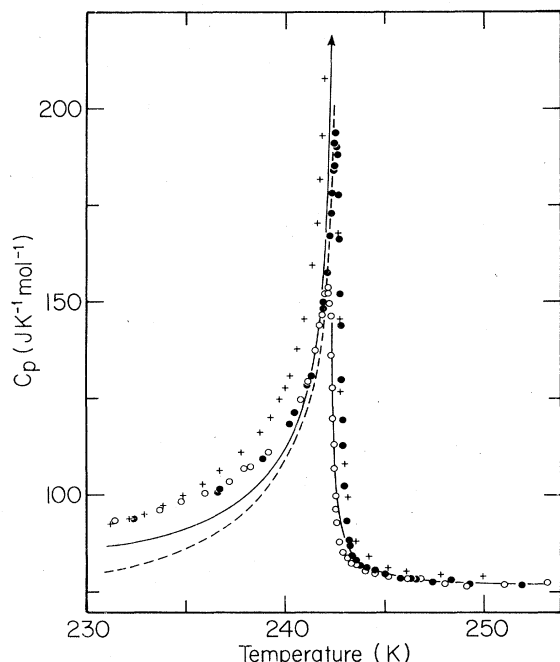


FIG. 1. Heat capacity of NH_4Cl at 1 atm. Solid and open circles indicate data taken increasing and decreasing the temperature, respectively. Values obtained by adiabatic calorimetry (Ref. 5) are indicated by "+" symbols. Smooth-curve values of Schwartz (Ref. 7) are shown for his sample 2 (solid curves) and sample 3 (dashed curve).

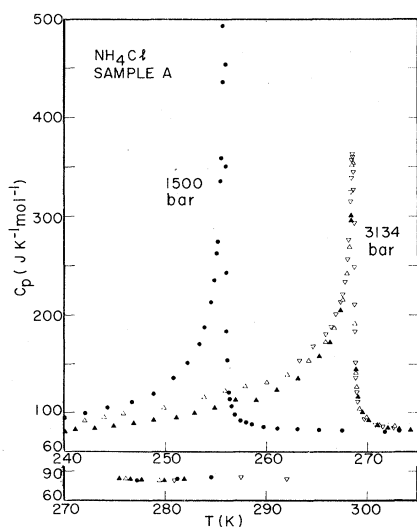


FIG. 2. Heat capacity of NH_4Cl at 1500 bar (solid dots) and 3134 bar (triangles: solid for the first run, open for the second, and inverted for the third).

it is clear that the two sets of data differ below the transition. The smooth curves in Fig. 1 representing the ac calorimetry results of Schwartz⁷ will be discussed in Sec. IV.

Several high-pressure warming runs were made on single-crystal NH_4Cl (sample A) over the range 240–290 K. The results are shown in Fig. 2, for which the calibration factor ν was taken to be 0.844 at 1500 bar and 0.904 at 3134 bar.¹⁷ Two runs at 1500 bar were in excellent internal agreement over the entire range and the data points from both these runs are shown without distinction in Fig. 2. However, the three warming runs at 3134 bar are distinguished by different symbols. Although all three sets of C_p values superimpose (to within $\pm 1.5\%$) above the transition temperature, there are systematic differences in the C_p values obtained below the transition. For the second and third runs, the low-temperature C_p values were found to be about $7 \text{ J K}^{-1} \text{ mol}^{-1}$ larger than those for the preceding run although the transition temperature did not change. It should be noted that the heat-capacity curves in the ordered phase can be superimposed by making additive shifts in C_p . Thus, the temperature dependence of C_p is essentially identical for all three runs.

Figure 2 does not fully represent the difference in the peak C_p values at 1500 and 3134 bar, since there are 11 data points at 1500 bar corresponding to $C_p > 500 \text{ J K}^{-1} \text{ mol}^{-1}$, with the largest observed

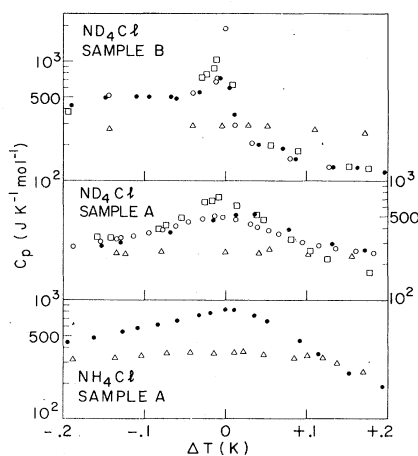


FIG. 3. Detailed view of the heat-capacity variation in the transition region for NH_4Cl and ND_4Cl . In the case of NH_4Cl , the solid circles represent data at 1500 bar and the triangles represent data at 3134 bar. For both samples of ND_4Cl , the solid circles are 1-atm warming values and the open circles are 1-atm cooling values. The triangles represent data taken subsequently on these samples at 1500 bar, and the open squares are data taken at 1 atm after the sample had been cycled in pressure.

value being $8300 \text{ J K}^{-1} \text{ mol}^{-1}$. A close-up view of the heat capacity peaks for this sample is shown in Fig. 3, where a plot of $\log_{10} C_p$ vs $T - T(\text{max})$ has been used for a convenient display of the detailed behavior. Although the two NH_4Cl curves are essentially identical for $\Delta T > +0.1 \text{ K}$ and differ only slightly when $\Delta T < -0.25 \text{ K}$ (see Sec. IV), there is an appreciable flattening of the peak region at 3134 bar. This "rounding" of the data points near the transition at high pressures is consistent with previous measurements of NH_4Cl compressibility¹ and differential thermal analysis curves.¹⁰ We shall show in connection with our measurements on ND_4Cl that this rounding is a reversible effect.

ND_4Cl results. The heat-capacity data taken on ND_4Cl sample A at 1 atm and 1500 bar are displayed in Fig. 4. Also shown are the 1-atm adiabatic calorimeter data of Stephenson.³ Our 1-atm C_p values were tied to Stephenson's value of $88.5 \text{ J K}^{-1} \text{ mol}^{-1}$ at 280 K by using $\gamma = 1.000$. As can be seen, the agreement between the two sets of data is generally quite good over the entire temperature range investigated. However, our C_p values are consistently smaller than those of Stephenson by 5 to $10 \text{ J K}^{-1} \text{ mol}^{-1}$ in the range 240–250 K. Our 1-atm C_p values for sample A were reproducible on two warming and two cooling runs to within $\pm 0.5\%$ except for a region of about 1 K° on either side of

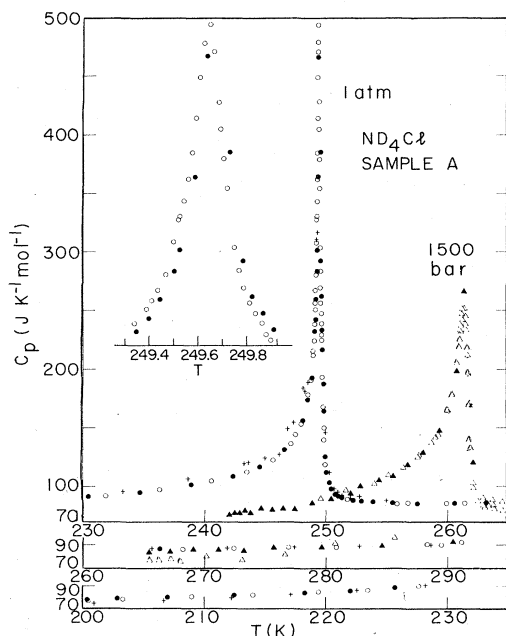


FIG. 4. Heat capacity of ND_4Cl (sample A) at 1 atm and 1500 bar. Solid and open circles represent 1-atm data obtained on warming and cooling runs, respectively. Solid and open triangles represent data from several warming runs at 1500 bar. 1-atm data obtained by adiabatic calorimetry (Ref. 3) are represented by the symbol "+."

the peak. In this region a small hysteresis of about 30 mK was observed. This hysteresis can be seen clearly on the inset which displays the 1-atm peak region on an expanded temperature scale. For this sample, the C_p values close to the transition are remarkably symmetric about a peak value of $\sim 520 \text{ J K}^{-1} \text{ mol}^{-1}$.

Also shown in Fig. 4 are data taken on sample A at a constant pressure of 1500 bar. Three warming runs were made: the first high-pressure run is indicated by solid triangles in Fig. 4, while the combined data from the second and third runs are indicated by open triangles. The C_p values in the ordered phase differ from one run to another by less than 4%, which is also about the size of the scatter in the low-temperature data from the first run. The C_p values were better behaved in the vicinity of the peak, where the scatter was less and the values were reproducible to within $\pm 2\%$. However, the C_p values obtained above 265 K on the second and third runs are $\sim 10 \text{ J K}^{-1} \text{ mol}^{-1}$ lower than those from the first run and display more scatter. The same calibration factor $\gamma = 0.979$ was used for all three 1500-bar runs, and this value corresponds to tying our first run to Stephenson's value at 280 K.

A detailed comparison of the heat capacity peaks for ND_4Cl sample A at 1 atm and 1500 bar is given in Fig. 3. The overall variation in C_p due to the order-disorder transition is quite similar in magnitude at both pressures (see Sec. IV) except for the very clear rounding of the peak values at 1500 bar. After completion of the 1500-bar runs, the pressure was reduced to 1 atm and the transition region was investigated again. These data, represented by the open squares in Fig. 3, indicate that the change in peak C_p values with pressure is essentially reversible. The heat-capacity values obtained after pressure cycling were within 2% of those prior to pressurizing except for the region just above the transition. As shown in Fig. 3, the new values are actually larger than the initial 1-atm values over an interval of $\pm 80 \text{ mK}$ about the peak. In the range from 0.08 to 1 K above the peak, the new values are smaller than the initial ones. Thus, although there are some small irreversible changes as a result of pressure cycling, the major rounding of the C_p peak at 1500 bar is a reversible change.

The results of a series of runs on a second sample, ND_4Cl sample B, are displayed in Fig. 5. The data of Stephenson³ are again shown for comparison. Our data were tied to Stephenson's value at 280 K using $\gamma = 1.217$. Once again, overall agreement with the adiabatic calorimetry values is reasonably good, especially in the transition region. However, our C_p values below 235 K are systematically larger than Stephenson's values. Note that

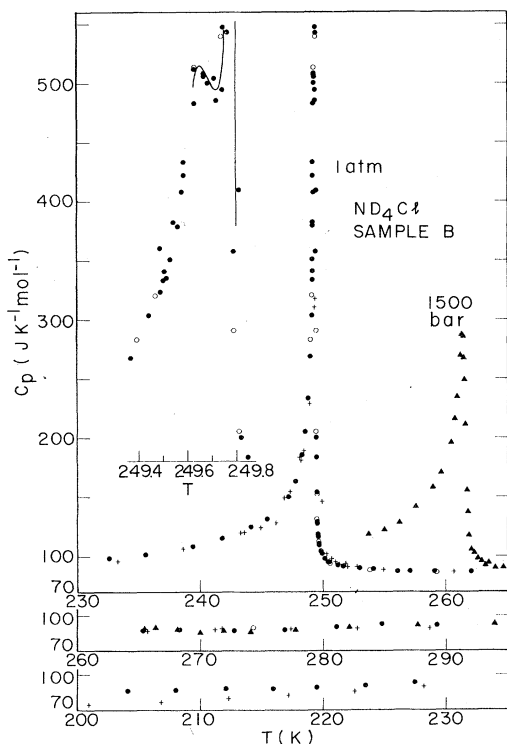


FIG. 5. Heat capacity of ND_4Cl (sample B) at 1 atm and 1500 bar. 1-atm warming data are shown as solid circles while cooling data are shown as open circles. Solid triangles represent data taken at 1500 bar. 1-atm values obtained by adiabatic calorimetry (Ref. 3) are shown by the symbol "+".

the deviations from Stephenson differ for samples A and B. This is due to the fact that our C_p values in the ordered phase are higher for sample B than those for sample A by approximately $7 \text{ J K}^{-1} \text{ mol}^{-1}$ throughout the range 200–250 K. For sample B, no discernible temperature hysteresis was observed on two warming and two cooling runs. An expanded plot of the peak region (see the inset on Fig. 5) shows that the behavior of this sample below 249.65 K is quite similar to that observed with sample A. However, the behavior at higher temperatures is very different, with a small decrease in C_p followed by a sharp increase and an even more abrupt drop. This feature (indicated by a light line through the points) was observed on both warming runs and is consistent with the few data points in this region obtained on cooling. Data taken at 1500 bar on sample B are also shown in Fig. 5. These data were tied to Stephenson's value using $\gamma = 1.207$. As with sample A, the most obvious effect of pressure has been to drastically reduce the peak values of C_p .

A comparison of heat-capacity peaks obtained from 1-atm and 1500-bar runs on this sample is

shown in Fig. 3, where differences in the 1-atm behavior of samples A and B are readily apparent on the high-temperature side of the maximum. However, sample-B data taken after pressure cycling are found to be in good agreement with data taken before pressure is applied to the crystal. Thus the significant reduction in the peak C_p value when the pressure is raised from 1 atm to 1500 bar has again been shown to be a reversible effect.¹⁸

IV. DISCUSSION

Before presenting an analysis of our data in terms of critical-exponent values, it is appropriate to comment on some general features of the results. The 1-atm data on NH_4Cl are mainly of interest since it is possible to make detailed comparisons with previous work. Figure 1 allows a comparison of adiabatic calorimetry results with our results and those of Schwartz, whose data were also obtained on single-crystal slabs using the ac method. (The smooth curves representing Schwartz's data were obtained by reading values from the figures given in Ref. 7.) The C_p variations that we observe in the disordered phase are quite consistent with the results of these other investigations. Our warming data agree well with the adiabatic data, which were taken on warming as usual. Our cooling data agree with Schwartz's cooling run on his sample 2, although the agreement in the "plateau" region around 250 K is not significant since Schwartz's values were converted from arbitrary to SI units by tying his data to the value $78.1 \text{ J K}^{-1} \text{ mol}^{-1}$ at 247 K. In the ordered phase, the situation is less satisfactory. Our C_p values are reproducible over several runs on a single sample, but differ from those obtained by Schwartz on warming runs. Although it is not possible to judge the reproducibility of his data on a given crystal, a sample dependence is obvious. In the case of Schwartz's sample 2, the C_p values lie uniformly below our values by $6.0 \text{ J K}^{-1} \text{ mol}^{-1}$ in the 230–240 K range (which is similar to the shift we observed between ND_4Cl samples A and B), but lie above our values close to the transition. In spite of such sample-dependent differences, the ac calorimetry results all show the same kind of systematic deviations from the data of Amitin *et al.* The "width" on an ac heat-capacity peak is appreciably less than that obtained from adiabatic measurements. Since three independent adiabatic calorimeter experiments³⁻⁵ agree with each other to within 1% or better, this difference in C_p variation must be a real effect. The origin of such a difference is not clear, but may possibly be related to the fact that single crystals of NH_4Cl were used in the ac experiments and rather finely divided pow-

ders were used in the adiabatic experiments. Schwartz has reported that the peak C_p values were sensitive to sample treatment,⁷ while Thomas and Stavely have found some effects of particle size on the thermal expansion of NH₄Cl powders.¹⁹

In the case of ND₄Cl the adiabatic calorimeter data are not as detailed as those for NH₄Cl, but Figs. 4 and 5 suggest that the same sort of systematic differences do not exist between adiabatic and ac results. The present results indicate that the detailed behavior of C_p in the immediate vicinity of the transition is definitely sample dependent although reproducible for several runs on a given sample. Similar anomalous behavior was observed in measurements of the piezoelectric constant and thermal expansion of ND₄Cl single crystals.² Furthermore the heat-capacity variation just above the transition (up to 1.5 K above the temperature of the peak) is not well characterized. Not only is the behavior sample dependent, but the C_p values in this range are not as reproducible from run to run. (In the case of sample A, pressure cycling had a distinct effect.) Therefore, no power-law fits will be attempted for the data in the disordered phase.

The heat-capacity variation in the ordered phase of NH₄Cl and ND₄Cl has been analyzed in terms of the expression

$$\Delta C_p \equiv C_p - C_p(\text{background}) = A' t^{-\alpha'} \quad (3)$$

where ΔC_p is the configurational contribution, t is the reduced temperature $|T - T_c|/T_c$, and α' is the critical exponent for data below T_c . As usual the maximum heat capacity is rounded off at some finite value in all samples and data very close to the peak could not be used in the fitting procedure.

This unfortunately introduces some uncertainty in the value of T_c , and T_c was treated as a parameter to be varied over a narrow range in order to find the best fit. A least-squares-fitting procedure was used to minimize χ_p^2 with A' and α' treated as freely adjustable parameters for a fixed background heat capacity and for various fixed values of T_c covering a 200-mK range about the temperature of the peak.

Two plausible choices of background were used. In the first choice, a smooth interpolation curve was drawn connecting the adiabatic calorimeter data far below the transition (140 K and below) to data considerably above (275 K and above). Although an interpolation of this type must necessarily be curved in order to join smoothly at both ends of the range, it can be well represented over the interval 200–250 K by a straight line. The interpolation choice corresponds to $C_p(\text{background}) = 74.9 - 0.22(250 - T)$ for NH₄Cl and $81.6 - 0.215(250 - T)$ for ND₄Cl, where SI units are used. The second background choice was a calculated heat-capacity

curve based on using a combination of Debye and Einstein functions determined by fitting the low-temperature (20–150 K) heat capacity data.³ Such a Debye-Einstein curve, which takes into account the lattice vibrations and the torsional oscillations of the ammonium ion, lies below the interpolation choice throughout the range of interest. In the 200–250 K region, this second choice can also be well represented by a linear variation: $C_p(\text{background}) = 64.2 - 0.11(250 - T)$ for NH₄Cl and $69.7 - 0.11(250 - T)$ for ND₄Cl. Fortunately, the character and the quality of the fits based on Eq. (3) were not highly sensitive to the choice of background. The Debye-Einstein background, which gave comparable or slightly smaller χ^2 values in every case, will be used henceforth. Use of the interpolation background would result in α' values which are a little larger (by ~ 0.05) and A' values which are considerably (about 30%) smaller.

Figure 6 shows \log_{10} - \log_{10} plots of ΔC_p vs t for all our measurements except those on NH₄Cl at 1 atm. The linearity of such a plot should indicate the quality of a power-law fit, but it should be noted that this linearity is sensitive to the choice of T_c at small- t values and to the choice of background at large t values. For NH₄Cl at 1500 bar the best fit was achieved with $T_c = T_0 + 0.05$ K, where T_0 is the temperature at the peak of the C_p curve. The corresponding critical exponent is $\alpha' = 0.57 \pm 0.07$, where the limits represent the values of the exponent when $T_c = T_0$ ($\alpha' = 0.5$) and $T_c = T_0$

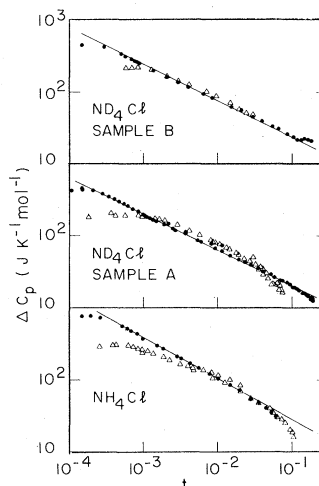


FIG. 6. \log_{10} - \log_{10} plots of ΔC_p vs t in the ordered phase. In the case of NH₄Cl, solid dots correspond to 1500 bar and triangles 3134 bar. For both samples of ND₄Cl, solid dots are 1-atm values and triangles are 1500 bar data. The lines represent the best power-law fits to the 1500-bar NH₄Cl data and the 1-atm ND₄Cl data.

+0.1 K ($\alpha' = 0.64$). For ND_4Cl at 1 atm the best fit gave $\alpha' = 0.50 \pm 0.07$ for both samples with $T_c = T_0 + 0.05$ K. In the analysis of sample *B*, the temperature T_0 was taken to correspond to the small peak at $513 \text{ JK}^{-1} \text{ mol}^{-1}$ and the unusual variation just above this peak was ignored.

Attempts to fit the 3134-bar data for NH_4Cl and the 1500-bar data for ND_4Cl samples show that there are systematic deviations from a simple power law, which is clear from the curvature of the plots in Fig. 6. This may indicate crossover behavior, but our data are not adequate to support such a claim. The qualitative feature of importance is the fact that the magnitude of the heat capacity is insensitive to pressure over the range $10^{-3} < |t| < 5 \times 10^{-2}$, but very pressure dependent in the region $|t| < 10^{-3}$ (see also Fig. 3).

In view of the observed hysteresis and the known first-order instability for NH_4Cl at 1 atm, it is doubtful whether one should attempt to fit such data with a simple power law. Nevertheless, Amitin *et al.*⁵ have carried out such a fit to their 1-atm NH_4Cl data. They cite a value $\alpha' = 0.44 \pm 0.07$ based on using data at large t ($0.04 < t < 0.25$) and the choice $T_c = T_0 + 1$ K; data in the range $0.007 < t < 0.04$ were fit separately and larger exponents (~ 0.6) were found. Schwartz⁷ has reported the value $\alpha' = 0.67$ for warming data on his sample 2. However, it should be pointed out that Schwartz (i) used a complicated fitting procedure with eight freely adjustable parameters, (ii) defined his reduced temperature by $t = (\Delta T/T_c) + n(\Delta V/V_c)$, where ΔV is strongly temperature dependent near T_c , and (iii) reported that equally good fits were found with parameter values which varied by 30% from those cited. This method of analysis may have a considerable effect on the value of α' since our attempt to reanalyze his data using Eq. (3) gave $\alpha' \approx 0.5$. For comparison, we have also used Eq. (3) to represent our warming data on NH_4Cl at 1 atm. The best fit is obtained if T_c is chosen to be $T_0(\text{warm}) + 0.3$ K, and the resulting exponent is $\alpha' = 0.4$. In addition to these calorimetric values of α' , Fredericks²⁰ has reported $\alpha' = 0.75$ from an analysis of his thermal-expansion data, using the same unusual fitting procedure as used by Schwartz. It seems unlikely that very much significance should be attached to any of these exponent values for NH_4Cl at 1 atm.

For NH_4Cl at high pressure, we can compare our results with the thermal expansion measurements of Weiner and Garland.¹ They analyzed the length variation of a large single crystal to obtain $\alpha' = 0.57$ at 1636 bar and $\alpha' = 0.40$ at 2841 bar. Furthermore, compressibility measurements at 255.95 K (for which $p_c = 1492$ bar) also gave $\alpha' = 0.57$. Thus, the agreement with our calorimetric value of

α' at 1500 bar is excellent (perhaps fortuitously close). The α' value 0.4 at 2841 bar is also quite consistent with our C_p data at 3134 bar; if the latter are fit over the limited range $7 \times 10^{-4} < t < 2 \times 10^{-2}$ (see Fig. 6), we obtain $\alpha' = 0.36$.

In the case of ND_4Cl , the only available exponent comparison is with thermal-expansion data at 1 atm.^{2(a)} That work also showed sample dependence in the detailed behavior very close to the transition, and the power-law analysis was based on using a T_c value that was 60 mK above the observed transition temperature. However, the reported value $\alpha' = 0.69 \pm 0.06$ is in serious disagreement with the value 0.50 ± 0.07 found here. Reference 2(a) was primarily an interferometric investigation of the piezoelectricity (order parameter) of ND_4Cl , and the interferometer was not ideally designed for thermal-expansion measurements. As a result there was considerable ambiguity in the choice of the linear background expansion coefficient, and the α' value was quite sensitive to this choice. Nevertheless, the discrepancy between the α' values obtained with these two independent methods is greater than expected.

Unfortunately, the critical exponents α' obtained in the present investigation do not clearly resolve the character of the multicritical point in ammonium chloride. The result for ND_4Cl at 1 atm is consistent with a tricritical point, but our α' value of 0.57 ± 0.07 for NH_4Cl at 1500 bar could correspond to either a tricritical point (for which $\alpha = \alpha' = \frac{1}{2}$ and $\beta = \frac{1}{4}$) or a fourth-order Gaussian point (for which $\alpha = \alpha' = \frac{2}{3}$ and $\beta = \frac{1}{6}$).²¹ The calorimetry work alone would favor a tricritical point, but the order-parameter exponents $\beta \approx 0.13$ from piezoelectric data² and $\beta \approx 0.15$ from neutron scattering measurements²² on $\text{N}(\text{D}_{0.93}\text{H}_{0.07})_4\text{Cl}$ are consistent with a Gaussian higher critical point. Furthermore, it is significant that the C_p variation just above the transition is sample dependent and, in any case, not well characterized by a power law with $\alpha = \alpha'$. In the case of ND_4Cl , the exponent γ seems to be close to 1.^{22, 23} If this is correct and $\gamma' = 1$ due to scaling, the Rushbrooke inequality yields $\alpha' + 2\beta \geq 1$, which is not satisfied by the α' and β values cited above. Perhaps there are smoothly varying changes in domain pattern throughout the ordered phase which distort the order parameter measurements and lead to erroneous β values, or perhaps fluctuations are not playing a dominant role even when the first-order character has apparently disappeared at the "multicritical" pressure. In the latter connection it should be noted that the behavior of the heat capacity strongly resembles that predicted near a classical tricritical point of the type called by Landau a "Curie critical point," as suggested previously in Ref. 1.

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- ¹B. B. Weiner and C. W. Garland, *J. Chem. Phys.* **56**, 155 (1972); see also C. W. Garland and B. B. Weiner, *Phys. Rev. B* **3**, 1634 (1971).
- ²(a) C. W. Garland, D. E. Bruins, and T. J. Greytak, *Phys. Rev. B* **12**, 2759 (1975); (b) D. E. Bruins and C. W. Garland, *J. Chem. Phys.* **63**, 4139 (1975).
- ³C. C. Stephenson (private communication of unpublished data).
- ⁴H. Chihara and M. Nakamura, *Bull. Chem. Soc. Jpn.* **45**, 133 (1972).
- ⁵E. B. Amitin, Yu. A. Kovalevskaya, E. G. Lebedeva, and I. E. Paukov, *Fiz. Tverd. Tela* **17**, 2549 (1975) [*Sov. Phys.-Solid State* **17**, 1699 (1976)].
- ⁶A. V. Voronel and S. R. Garber, *Zh. Eksp. Teor. Phys.* **52**, 1464 (1967) [*Sov. Phys.-JETP* **25**, 970 (1967)].
- ⁷P. Schwartz, *Phys. Rev. B* **4**, 920 (1971); and Ph.D. thesis (Univ. of Illinois, 1969) (unpublished).
- ⁸S. A. Zlunitsyn, *Zh. Eksp. Teor. Fiz.* **8**, 724 (1938).
- ⁹E. B. Amitin, Yu. A. Kovalevskaya, and I. E. Paukov, *Fiz. Tverd. Tela* **14**, 3483 (1972) [*Sov. Phys.-Solid State* **14**, 2902 (1973)].
- ¹⁰N. J. Trappeniers and Th. J. van der Molen, *Physica* **32**, 1161 (1966); Th. J. van der Molen, Ph.D. thesis (Univ. of Amsterdam, 1966) (unpublished).
- ¹¹J. D. Baloga and C. W. Garland, *Rev. Sci. Instrum.* (to be published).
- ¹²R. Renard and C. W. Garland, *J. Chem. Phys.* **45**, 763 (1966).
- ¹³C. W. F. T. Pistorius, *J. Chem. Phys.* **50**, 1436 (1969).
- ¹⁴W. Mandema and N. J. Trappeniers, *Physica* **76**, 123 (1974).
- ¹⁵W. Bausch and W. Waidelich, *Phys. Lett. A* **30**, 190 (1969).
- ¹⁶S. S. Sharma, *Proc. Indian Acad. Sci. A* **31**, 339 (1950).
- ¹⁷No measurements were made on this sample at 1 atm, and these γ values should not be directly compared with that for sample B.
- ¹⁸An additional confirmation of this reversible reduction of the peak C_p value with pressure was obtained from a series of measurements on a third ND₄Cl sample. Data were taken only in the immediate vicinity of the transition for isobars at 760, 1100, 1500, and 2730 bar. A smooth monotonic decrease in peak C_p values was observed with increasing pressure, and the 760 bar value was shown to be reproducible after pressure cycling. Our thanks to G. Kasting for carrying out this investigation.
- ¹⁹D. G. Thomas and L. A. K. Staveley, *J. Chem. Soc. Lond. A* **1951**, 1420 (1951).
- ²⁰G. E. Fredericks, *Phys. Rev. B* **4**, 911 (1971).
- ²¹T. S. Chang, G. F. Tuthill, and H. E. Stanley, *Phys. Rev. B* **9**, 4882 (1974).
- ²²W. B. Yelon and D. E. Cox, *Solid State Commun.* **11**, 1011 (1972); W. B. Yelon, D. E. Cox, P. J. Kortman, and W. B. Daniels, *Phys. Rev. B* **9**, 4843 (1974).
- ²³D. R. McKenzie and R. S. Seymour, *J. Phys. C* **8**, 1071 (1975).