

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 NH_4Cl powders.¹⁹

In the case of ND_4Cl the adiabatic calorimeter data are not as detailed as those for NH_4Cl , 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 ND_4Cl 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 NH_4Cl and ND_4Cl 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^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 NH_4Cl and $81.6 - 0.215(250 - T)$ for ND_4Cl , 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 NH_4Cl and $69.7 - 0.11(250 - T)$ for ND_4Cl . 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 $\log_{10}\text{-}\log_{10}$ plots of ΔC_p vs t for all our measurements except those on NH_4Cl 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 NH_4Cl 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 $T_c = T_0$

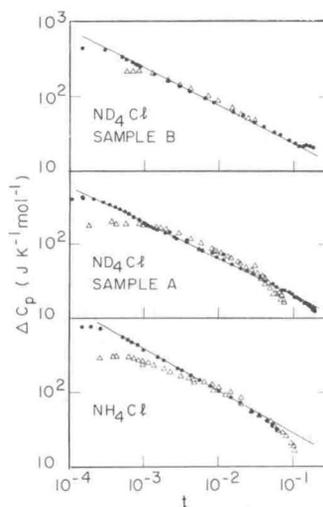


FIG. 6. $\log_{10}\text{-}\log_{10}$ plots of ΔC_p vs t in the ordered phase. In the case of NH_4Cl , solid dots correspond to 1500 bar and triangles 3134 bar. For both samples of ND_4Cl , solid dots are 1-atm values and triangles are 1500 bar data. The lines represent the best power-law fits to the 1500-bar NH_4Cl data and the 1-atm ND_4Cl 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.