

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  $\text{NH}_4\text{Cl}$  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  $\text{NH}_4\text{Cl}$  compressibility<sup>1</sup> and differential thermal analysis curves.<sup>10</sup> We shall show in connection with our measurements on  $\text{ND}_4\text{Cl}$  that this rounding is a reversible effect.

**$\text{ND}_4\text{Cl}$  results.** The heat-capacity data taken on  $\text{ND}_4\text{Cl}$  sample A at 1 atm and 1500 bar are displayed in Fig. 4. Also shown are the 1-atm adiabatic calorimeter data of Stephenson.<sup>3</sup> 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  $r = 1.000$ . 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  $1 \text{ K}^\circ$  on either side of

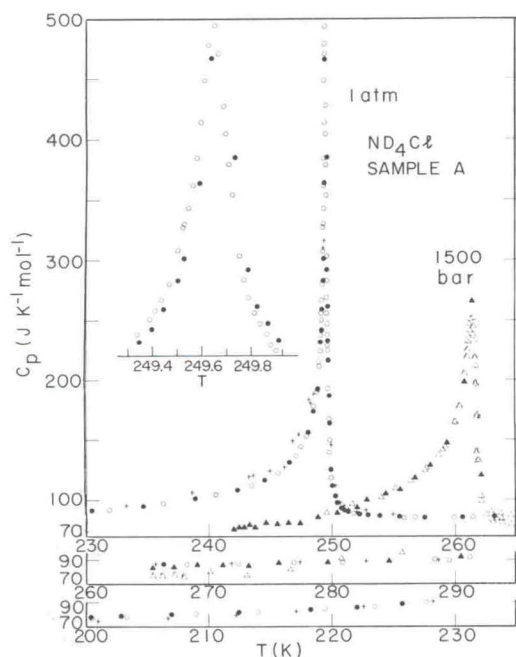


FIG. 4. Heat capacity of  $\text{ND}_4\text{Cl}$  (sample A) at 1 atm and 1500 bar. Solid and open circles represent 1-atm data obtained on warming and cooling runs, respectively. Solid and open triangles represent data from several warming runs at 1500 bar. 1-atm data obtained by adiabatic calorimetry (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  $r = 0.979$  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  $\text{ND}_4\text{Cl}$  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,  $\text{ND}_4\text{Cl}$  sample B, are displayed in Fig. 5. The data of Stephenson<sup>3</sup> are again shown for comparison. Our data were tied to Stephenson's value at 280 K using  $r = 1.217$ . 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

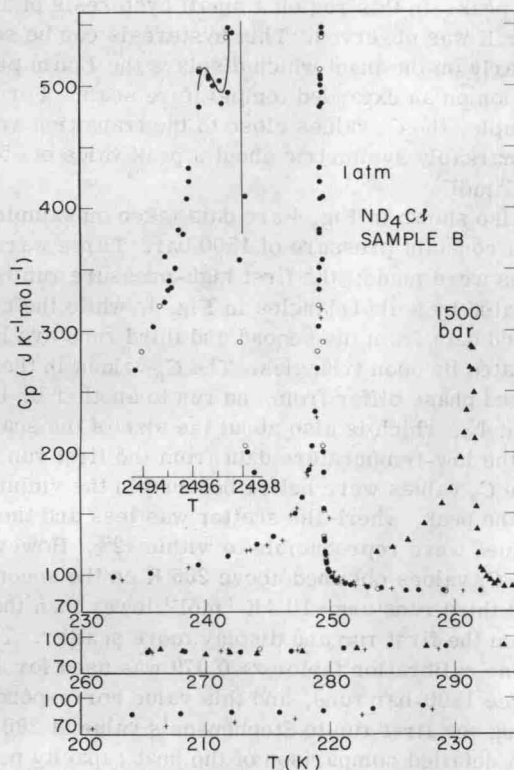


FIG. 5. Heat capacity of  $\text{ND}_4\text{Cl}$  (sample B) at 1 atm and 1500 bar. 1-atm warming data are shown as solid circles while cooling data are shown as open circles. Solid triangles represent data taken at 1500 bar. 1-atm values obtained by adiabatic calorimetry (Ref. 3) are shown by the symbol "+".

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  $7 \text{ JK}^{-1} \text{ mol}^{-1}$  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  $r = 1.207$ . 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.<sup>18</sup>

#### 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  $\text{NH}_4\text{Cl}$  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  $78.1 \text{ JK}^{-1} \text{ mol}^{-1}$  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  $6.0 \text{ JK}^{-1} \text{ mol}^{-1}$  in the 230–240 K range (which is similar to the shift we observed between  $\text{ND}_4\text{Cl}$  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 experiments<sup>3-5</sup> 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  $\text{NH}_4\text{Cl}$  were used in the ac experiments and rather finely divided pow-