

tions<sup>2-10, 12-14</sup> 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  $t \equiv |T - T_c|/T_c$ , 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  $\Delta T_{ac}$  was made. Indeed close to the transition the sample was equilibrated for  $\sim 2$  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  $0.01275 \text{ J K}^{-1}$  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  $\text{ND}_4\text{Cl}$  sample A,  $r = 1.217$  for  $\text{ND}_4\text{Cl}$  sample B, and  $r = 1.074$  for  $\text{NH}_4\text{Cl}$  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  $0.015 \text{ J K}^{-1}$ . This would lead to an increase of  $\sim 3\%$  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  $\gamma$  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  $\text{NH}_4\text{Cl}$  at 1 atm and 280 K,<sup>15</sup> and have found that this value and the ratio  $A_{eff}/A = 1.25$  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,  $\gamma$  was taken to be independent of temperature and pressure although the thermal conductivity data<sup>15</sup> at 1 atm indicate that  $\gamma$  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  $\gamma$  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  $\delta$ , which depends only on  $\omega$  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 coefficient<sup>16</sup> that  $(\partial C_p / \partial p)_T = -7.0 \times 10^{-4} \text{ J K}^{-1} \text{ mol}^{-1} \text{ bar}^{-1}$  for  $\text{NH}_4\text{Cl}$  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 40% of the sample heat capacity and these corrections are responsible for uncertainties of  $\sim 3\%$  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  $\text{ND}_4\text{Cl}$  sample A at 1500 bar and  $r = 1.207$  for  $\text{ND}_4\text{Cl}$  sample B at 1500 bar.

**$\text{NH}_4\text{Cl}$  results.** Two warming and two cooling runs were made on single-crystal  $\text{NH}_4\text{Cl}$  (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.*<sup>5</sup> 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 ( $\sim 3\%$ ) 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,



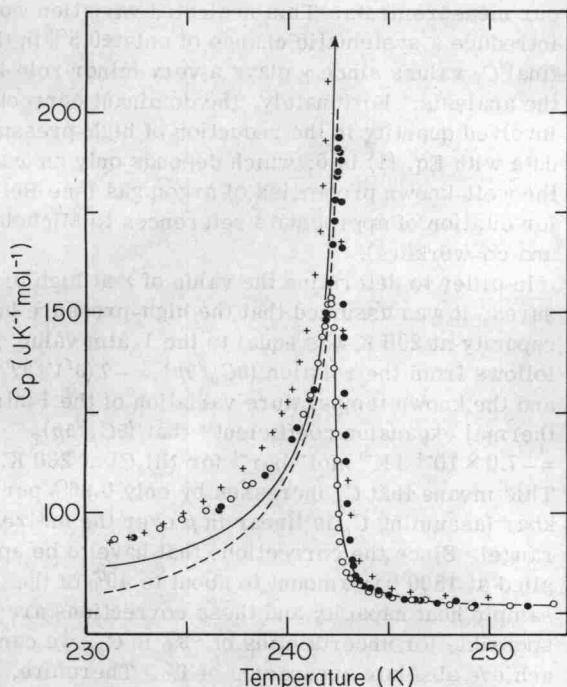


FIG. 1. Heat capacity of  $\text{NH}_4\text{Cl}$  at 1 atm. Solid and open circles indicate data taken increasing and decreasing the temperature, respectively. Values obtained by adiabatic calorimetry (Ref. 5) are indicated by "+" symbols. Smooth-curve values of Schwartz (Ref. 7) are shown for his sample 2 (solid curves) and sample 3 (dashed curve).

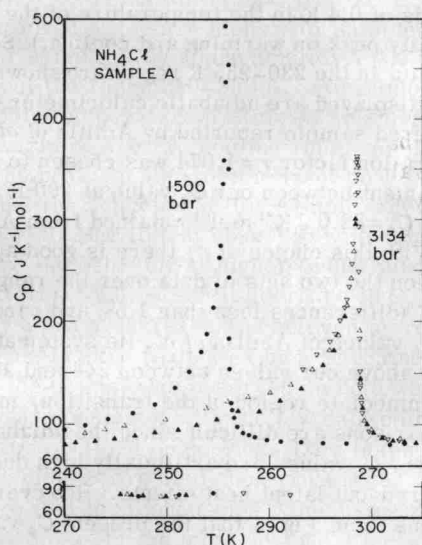


FIG. 2. Heat capacity of  $\text{NH}_4\text{Cl}$  at 1500 bar (solid dots) and 3134 bar (triangles: solid for the first run, open for the second, and inverted for the third).

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 Schwartz<sup>7</sup> will be discussed in Sec. IV.

Several high-pressure warming runs were made on single-crystal  $\text{NH}_4\text{Cl}$  (sample A) over the range 240–290 K. The results are shown in Fig. 2, for which the calibration factor  $\gamma$  was taken to be 0.844 at 1500 bar and 0.904 at 3134 bar.<sup>17</sup> 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

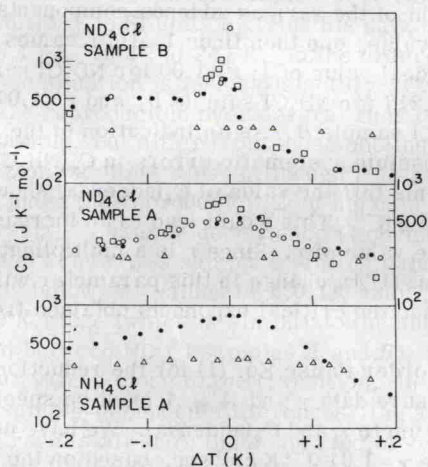


FIG. 3. Detailed view of the heat-capacity variation in the transition region for  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$ . In the case of  $\text{NH}_4\text{Cl}$ , the solid circles represent data at 1500 bar and the triangles represent data at 3134 bar. For both samples of  $\text{ND}_4\text{Cl}$ , 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.