

Heat capacity of  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$  single crystals at high pressure \*

C. W. Garland and J. D. Baloga

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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The constant-pressure heat capacity of  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$  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  $\sim 3$  kbar. The "multicritical" pressure (above which the transition is continuous and below which a small first-order instability occurs) is 1500 bar for  $\text{NH}_4\text{Cl}$  and is very close to 1 atm for  $\text{ND}_4\text{Cl}$ . A correspondence was found between the  $C_p$  variation for  $\text{ND}_4\text{Cl}$  at 1 atm and  $\text{NH}_4\text{Cl}$  at 1500 bar and also between that for  $\text{ND}_4\text{Cl}$  at 1500 bar and  $\text{NH}_4\text{Cl}$  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  $\text{ND}_4\text{Cl}$  and  $0.57 \pm 0.07$  for  $\text{NH}_4\text{Cl}$ . 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  $\text{NH}_4^+$  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.<sup>1</sup> Thus there is a high-pressure "multicritical" point in  $\text{NH}_4\text{Cl}$ . Furthermore, the first-order aspect of the transition is very sensitive to deuteration, and the multicritical point in  $\text{ND}_4\text{Cl}$  lies close to 1 atm.<sup>2</sup> The detailed nature of this multicritical point is not yet understood. Although formally similar to the tricritical point observed in metamagnets and  $^3\text{He}$ - $^4\text{He}$ , 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  $\text{NH}_4\text{Cl}$  at 1 atm. Stephenson,<sup>3</sup> Chihara and Nakamura,<sup>4</sup> and very recently Amitin *et al.*<sup>5</sup> 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 Garber<sup>6</sup> provide details about the hysteresis associated with the 1-atm transition, as does the ac calorimetry study of single-crystal samples by Schwartz.<sup>7</sup> 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 Schwartz<sup>7</sup> and by Amitin *et al.*,<sup>5</sup> 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  $\text{NH}_4\text{Cl}$  at high pressures<sup>8-10</sup> have not provided reliable quantitative data. In the case of  $\text{ND}_4\text{Cl}$ , there has been very little previous work on heat capacities. There are unpublished adiabatic calorimetry measurements by Stephenson<sup>3</sup> on powdered  $\text{ND}_4\text{Cl}$  samples from 20 to 300 K at 1 atm, and there are differential thermal analysis measurements by Trappeniers and van der Molen,<sup>10</sup> who carried out 1-atm and high-pressure studies of both  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$ .

The present investigation involves measurements of the isobaric heat-capacity variation for both  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$  single crystals at 1 atm and at high pressures. The resulting data are analyzed to obtain critical exponents  $\alpha'$  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  $\sim 3$  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,<sup>11</sup> 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  $\Delta T_{ac}$ . 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]

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

The quantity  $r$  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  $\rho_1$  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.<sup>11</sup> 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.<sup>11</sup> 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  $\Delta T_{ac}$ . The frequency  $\omega$ , 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  $\Delta T_{ac}$  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  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$  (99.2% deuteration) used in this investigation were the same as those used previously for piezoelectric measurements.<sup>2</sup> 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 cell<sup>11</sup> were carried out over the range 240–300 K, and the bath temperature could be held constant to within  $\pm 5$  mK over a period of 5 h. For measurements at 1 atm, a separate calorimeter somewhat similar to that described by Schwartz<sup>7</sup> 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 ( $\pm 2$  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  $\Delta T_{dc}$ .<sup>11</sup> 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-