

# Critical behaviour of the specific heat and the thermal expansion close to the melting point in ammonia solid III

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## Abstract

A linear correlation between the specific heat  $C_P$  and the thermal expansion  $\alpha_p$  is established here for constant temperatures close to the melting pressure in ammonia solid III. For this correlation, the experimental data for the isothermal compressibility  $\kappa_T$  is analysed according to a power-law formula with the critical exponent  $\gamma$  and, the  $C_P$  and  $\alpha_p$  are calculated as a function of pressure near the melting point in ammonia solid III.

Values of the entropy changes with the temperature, which are extracted from linear plots of  $C_P$  against  $\alpha_p$ , decrease as the temperature increases for the ammonia solid III prior to melting.

## Keywords

Specific heat · thermal expansion · melting point · ammonia solid III.

## 1 Introduction

Ammonia has three solid phases, namely, I, II and III with the different crystal structures, as determined experimentally [1]-[4]. Ammonia solid I has four molecules per unit cell in a cubic structure with the space group  $P_{213}$  [1]-[3], whereas ammonia solid II has two orientationally disordered molecules per unit cell in a hexagonal close-packed structure (hcp) with the space group  $P_{63}/mmc$  [4]. The third solid phase which exists at 35 kbar at 25 °C, has a face centered cubic (fcc) structure [5].

The Raman spectra of ammonia solid I [6] and II [7]-[10] have been obtained and the temperature dependence of the Raman frequencies for the lattice modes of solid I [6] and solid II [10] have been determined experimentally. Also, the pressure dependence of the Raman frequencies for the lattice modes has been obtained experimentally for the ammonia solid II [8]. We have calculated the Raman frequencies of two translational modes and one librational mode as a function of pressure close to the melting point in ammonia solid I [11]. For ammonia solid II, we have also calculated the Raman frequencies of a rotatory lattice (librational) mode as a function of temperature for constant pressures near the melting point in our previous study [12].

Phase diagrams containing the solid I, II and III phases of ammonia have been obtained from the experimental measurements as P-T phase diagrams [5, 8, 13] and a V-T phase diagram [6] in the literature. We have also calculated P-T phase diagram of solid I and II with the melting curves in ammonia [14] and T-P phase diagram of solid I, II and III phases [15] using the mean field theory. The experimental P-T phase diagram of ammonia [5, 8], as given in Fig. 1, shows that phase III melts directly as the pressure decreases, for example, from 0,9 GPa at a constant temperature of 280K. The experimental data for the measurements of the molar volume  $V$  and the isothermal compressibility  $\kappa_T$  of ammonia as a function of pressure, which we analyzed in this study, were taken at constant temperatures within the P-T range where phase III solid ammonia exists [16].

Near the melting point, it has been obtained that the isothermal compressibility  $\kappa_T$  of ammonia exhibits a divergence behaviour [5], [16]. We have also investigated the critical behaviour of ammonia (solid I and II) near the melting point in

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our earlier study [17]. By correlating the specific heat  $C_p$  with the thermal expansion  $\alpha_p$  (first Pippard relation) and the thermal expansion  $\alpha_p$  with the isothermal compressibility  $\kappa_T$  (second Pippard relation), we have established the Pippard relations in ammonia solid I and II close to the melting point [18]. We have also established the spectroscopic modification of the Pippard relation which relates the specific heat  $C_p$  to the frequency shifts  $(1/\nu) (\partial\nu/\partial T)_P$  for the rotatory [19] and translatory [20] lattice modes in ammonia solid II near the melting point.

In high pressure research, high pressure measurements of phase properties are essential for those which undergo phase transitions. Since ammonia solid III exists at high pressures, its phase properties, in particular, thermodynamic properties should be determined. Thus, predictions for the critical behaviour of the thermodynamic quantities prior to melting in ammonia solid III, as given in this study, can be examined by the high pressure measurements performed for this crystalline system. As an application, this should be of interest to study ammonia solid III in the high pressure research work.

We study here the pressure dependence of the thermodynamic quantities such as the specific heat  $C_p$ , thermal expansion  $\alpha_p$  and the isothermal compressibility  $\kappa_T$  near the melting point for ammonia solid III. Since ammonia solid III exhibits anomalous behaviour prior to melting such as ammonia I and II, it is interesting to study this material to investigate its critical behaviour. Our work given here is based on the experimental results of Pruzan et al. [16,21] for ammonia solid. Thus, the experimental data for the pressure dependence of the isothermal compressibility  $\kappa_T$  [16] at three constant temperatures (254.6, 274.0 and 297.5K) is analyzed according to a power-law formula and the values of the critical exponent  $\gamma$  for  $\kappa_T$  are extracted. Using the expressions for the pressure dependence of the thermal expansivity  $\alpha_p$  and of the specific heat  $C_p$  which we have also derived in our recent study on carbon tetrachloride [22], we calculate here  $\alpha_p$  and  $C_p$  as a function of pressure for the three constant temperatures considered near the melting point for ammonia solid III. By plotting  $C_p$  against the  $\alpha_p$ , we examine the first Pippard relation near the melting point in ammonia solid III.

Below, we give our calculations and results for  $\alpha_p$  and  $C_p$  close to the melting point in ammonia solid III, in section 2. We discuss our results in section 3. Finally, conclusions are given in section 4.

## 2 Calculations and results

The isothermal compressibility  $\kappa_T$  which is defined as

$$\kappa_T \equiv -(1/V)(\partial V/\partial P)_T \quad (1)$$

can be expressed as a function of pressure near the melting pressure  $P_m$  by a power-law formula,

$$\kappa_T = k(P - P_m)^{-\gamma} \quad (2)$$

where  $\gamma$  is the critical exponent,  $k$  is the amplitude of the isothermal compressibility. Near the melting point, variation of the melting pressure  $P_m$  with the temperature can be written approximately [16],

$$[P - P_m(T)]/[T_m(P) - T] = dP_m/dT \quad (3)$$

By means of Eq. (3), the isothermal compressibility  $\kappa_T$  can be written as a function of temperature

$$\kappa_T = k(dP_m/dT)^{-\gamma} (T_m - T)^{-\gamma} \quad (4)$$

The thermal expansion  $\alpha_p$  which is defined as

$$\alpha_p \equiv (1/V)(\partial V/\partial T)_P \quad (5)$$

can also be expressed as functions of pressure and temperature. Using Eq. (2) in the thermodynamic relation

$$\alpha_p/\kappa_T = dP_m/dT \quad (6)$$

the thermal expansion  $\alpha_p$  can be obtained as a function of pressure,

$$\alpha_p = k(dP_m/dT)(P - P_m)^{-\gamma} \quad (7)$$

Similarly, by using Eq. (4) in Eq. 6, the thermal expansion  $\alpha_p$  can be obtained as a function of temperature,

$$\alpha_p = k(dP_m/dT)^{1-\gamma} (T_m - T)^{-\gamma} \quad (8)$$

The temperature and pressure dependencies of the specific heat  $C_p$  can also be derived from the above relations. By writing the thermodynamics relation;

$$(\partial P/\partial T)_S = C_p/(TV\alpha_p) \quad (9)$$

and approximating

$$(\partial P/\partial T)_V = dP_m/dT = (\partial P/\partial T)_S \quad (10)$$

close to the melting point for ammonia [16], the pressure dependence of the specific heat  $C_p$  can be obtained as

$$C_p = TV(P)\alpha_p(dP_m/dT) \quad (11)$$

In Eq. (11) the pressure dependence of the thermal expansion  $\alpha_p$  is given by Eq. (7) and the volume  $V$  depends upon the pressure as

$$V(P) = V_c \exp[-k(1-\gamma)^{-1}(P - P_m)^{-1-\gamma}] \quad (12)$$

which can be derived from the definition of the isothermal compressibility Eq. (1). In Eq. (12)  $V_c$  denotes the critical volume as the critical point is close to the melting point for ammonia solid III. Similarly, the temperature dependence of the specific heat can be obtained as

$$C_p(T) = TV(T)\alpha_p(T)(dP_m/dT) \quad (13)$$

where  $\alpha_p(T)$  is given by Eq. (8) and

$$V(T) = V_c \exp[-k(1-\gamma)^{-1}(dP_m/dT)^{1-\gamma} (T_m - T)^{1-\gamma}] \quad (14)$$

Eq. (14) can also be derived from the definition of thermal expansion Eq. (5). Finally, by knowing the temperature and pressure dependencies of the thermal expansion  $\alpha_p$ , and the specific heat  $C_p$ , we are able to establish the Pippard relation near the melting point for ammonia solid III. This relates linearly the specific heat  $C_p$  to the thermal expansion  $\alpha_p$  near the melting point in ammonia solid III.

As derived by Pippard on the basis of a cylindrical approximation to the form of the entropy and volume surfaces in the vicinity of the  $\lambda$ -point and applied to the  $\text{NH}_4\text{Cl}$  [23], we derive it for the specific heat  $C_p$  and the thermal expansion  $\alpha_p$  of ammonia solid III near its melting point. Following Pippard [23], the entropy surface can be approximated to

$$S = S_m(P) + f(P - \Lambda T) \quad (15)$$

In a given pressure range, where  $\Lambda = dP_m/dT$  is the slope of the melting line.  $S_m$  represents the entropy value at the melting temperature  $T_m$ , which varies smoothly with the pressure (contains no quadratic or higher terms [23]). Since the slope  $\Lambda$  is constant at the melting point, the second derivative of the entropy with respect to the temperature and pressure yields

$$\left(\frac{\partial^2 S}{\partial T^2}\right)_P = \Lambda^2 f'', \quad \left(\frac{\partial^2 S}{\partial T \partial P}\right) = -\Lambda f'', \quad \left(\frac{\partial^2 S}{\partial P^2}\right)_T = f'' \quad (16)$$

where  $f''$  is the second derivative of  $f$  with respect to its argument. Eq. (16) gives rise to the relation

$$\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial T}\right)_P = \Lambda \frac{\partial}{\partial T} \left(\frac{\partial V}{\partial T}\right)_P \quad (17)$$

and

$$\frac{\partial}{\partial P} \left(\frac{\partial S}{\partial T}\right)_P = \Lambda \frac{\partial}{\partial P} \left(\frac{\partial V}{\partial T}\right)_P \quad (18)$$

using the thermodynamic relation

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \quad (19)$$

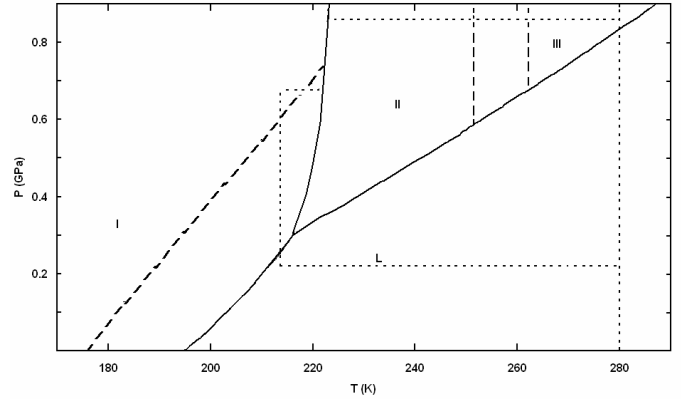
By integrating Eq. (17) or Eq. (18) and using the definition of the specific heat

$C_p = T(\partial S/\partial T)_P$  and the thermal expansion  $\alpha_p$  Eq. (5), we finally obtain the Pippard relation as

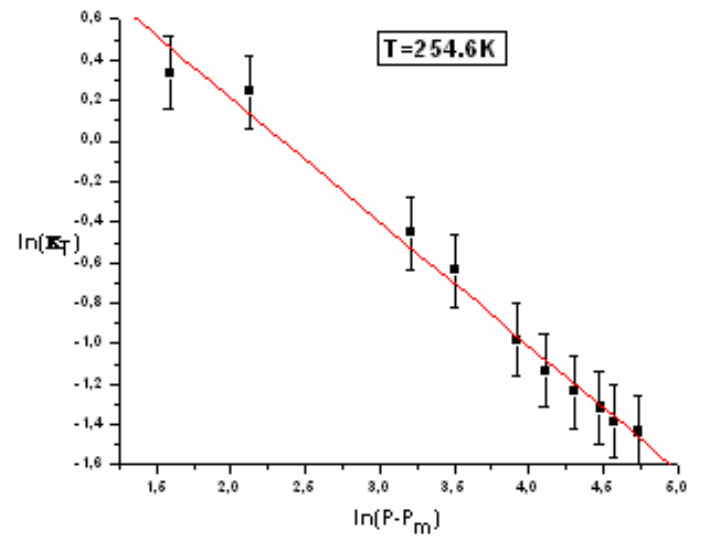
$$C_p = TV(dP_m/dT)\alpha_p + T(dS/dT)_m \quad (20)$$

with the slope  $\Lambda = dP_m/dT$  and the integration constant  $T(dS/dT)_m$ . In Eq. (20),  $(dS/dT)_m$  represents the variation of the entropy  $S$  with the temperature at the melting point for ammonia solid III.

In order to examine the Pippard relation Eq. (15), we started by analysing the experimental data for the isothermal compressibility  $\kappa_T$  as a function of pressure for the fixed temperatures at 254.6, 274 and 297.5K [16] close to the melting pressure in ammonia solid III. From our analysis, the pressure dependence of the isothermal compressibility  $\kappa_T$  is plotted in a log-log scale

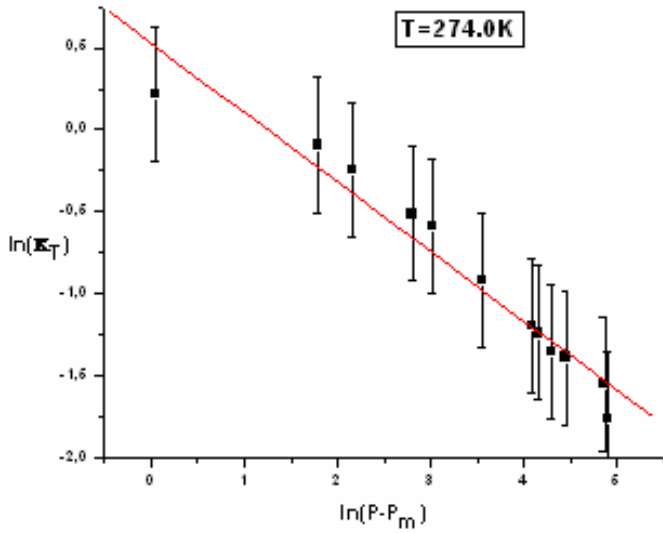


**Fig. 1.** Phase diagram of ammonia: ———— solid lines: melting curve and transition line I-II [5]. - - - - - broken line: appearance of sound signal on lowering  $T$  or raising  $P$  [5]. - - - - - thin broken line: transition zone II-III [8]. ······ dotted line: range of the previous investigation [8]. This phase diagram of ammonia is taken from Ref. [8].

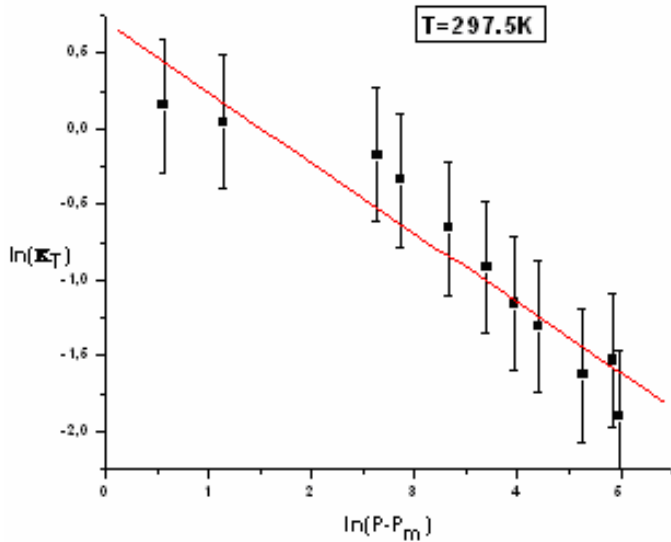


**Fig. 2.** A log-log plot of the isothermal compressibility  $\kappa_T$  as a function of  $P-P_m$  for 254.6K from the analysis of the experimental data [16] according to Eq. (2) close to the melting pressure  $P_m$  in ammonia solid III. Uncertainties in  $\kappa_T$  are also indicated here.

for constant temperatures at 254.6, 274 and 297.5K in Figs. (2-4), respectively. By determining the values of the critical exponent  $\gamma$  for  $\kappa_T$  and the amplitude  $k$  for the three fixed temperatures considered according to the power-law formula Eq. (2), the thermal expansion  $\alpha_p$  and the specific heat  $C_p$  were calculated as a function of pressure by Eqs. (7) and (11), respectively. In Eq. (11) the pressure dependence of the molar volume was calculated from Eq. (12). Thus, the experimental data for the  $\kappa_T$  [16] was analyzed and the values of  $\gamma$  and  $k$  were determined using Eq. (2), as tabulated in Table 1 for fixed temperatures at 254.6, 274 and 297.5K in ammonia solid III. Using the experimental value of  $dP_m/dT = 13 \text{ MPa/K}$  [16], the pressure dependence of thermal expansion  $\alpha_p$  was then evaluated by Eq. (7) with the values of  $\gamma$  and  $k$  for the fixed temperatures considered (Table 1) here in ammonia solid III. We also evaluated the molar volume at various pressures in the same pressure interval for the analysis for the fixed temperatures at 254.6, 274 and 297.5K



**Fig. 3.** A log-log plot of the isothermal compressibility  $\kappa_T$  as a function of  $P - P_m$  for 274K from the analysis of the experimental data [16] according to Eq. (2) close to the melting pressure  $P_m$  in ammonia solid III. Uncertainties in  $\kappa_T$  are also indicated here.



**Fig. 4.** A log-log plot of the isothermal compressibility  $\kappa_T$  as a function of  $P - P_m$  for 297.5K from the analysis of the experimental data [16] according to Eq. (2) close to the melting pressure  $P_m$  in ammonia solid III. Uncertainties in  $\kappa_T$  are also indicated here.

close to the melting point in ammonia solid III, according to Eq. (12). Therefore, the pressure dependence of specific heat  $C_P$  was calculated by knowing the pressure dependence of the thermal expansion  $\alpha_p$  and the volume  $V$  for constant temperatures at 254.6, 274 and 297.5K, according to Eq. (11) in ammonia solid III.

Since we obtained the pressure dependence of the specific heat  $C_P$  and thermal expansion  $\alpha_p$  at constant temperatures studied, we then plotted  $C_P$  against  $\alpha_p$  according to the Pippard relation (Eq. (15)). Our plots for the constant temperatures at 254.6, 274 and 297.5K close to the melting point in ammonia solid III, are given in Figs. 5-7, respectively. In Table 1, we give the values of the intercept  $(dS/dT)_m$  at the melting point, which

we extracted from our plots (Figs. 5-7 according to Eq. (15).

### 3 Discussion

The specific heat  $C_P$  and the thermal expansion  $\alpha_p$  which we calculated here at various pressures vary linearly, as plotted in Figs. 5-7 for constant temperatures at 254.6, 274 and 297.5K, respectively close to the melting in ammonia solid III. This linear variation of the specific heat  $C_P$  with the thermal expansion  $\alpha_p$  indicates that both thermodynamic functions exhibit similar critical behaviour near the melting point in ammonia solid III. According to the  $\gamma$  values (Table 1) the critical behaviour of  $C_P$  and  $\alpha_p$  is closer for constant temperatures at 274K (Fig. 6) and 297.5K (Fig. 7). The experimental uncertainties from the measurements of the isothermal compressibility  $\kappa_T$  as a function of pressure, which was considered in our analysis given here (Figs. 2-4), also occur as uncertainties in the thermal expansion  $\alpha_p$  and in the specific heat  $C_P$ . When the specific heat  $C_P$  is plotted against  $\alpha_p$  by considering uncertainties in both functions, a linear variation for constant temperatures at 254.6, 274 and 297.5K does not vary significantly, as shown in Figs. 5-7), respectively with the same slope of  $dP_m/dT = 13\text{MPa/K}$ . Considering the exponent values that vary from 0.4 to 0.6 (Table 1), ammonia solid III exhibits a second-order phase transformation prior to melting, as suggested for ammonia solids I and II [16]. The second-order transition in ammonia proceeds up to first-order melting [16]. This transformation may be due to an orientational disorder [21]. So that the specific heat  $C_P$  and the thermal expansion  $\alpha_p$  show anomalous behaviour near the melting point, which can be related to the orientational motion of  $\text{NH}_3$  molecules in the ammonia solid III. The reorientation of  $\text{NH}_3$  molecules is in fact due to the progressive breaking of the weak hydrogen bonds in ammonia solid III. This breaking of hydrogen bonds may account for a dramatic softening of solid ammonia on approach to melting [21]. Thus, the hydrogen bond distortion can occur by thermal motion near the melting point in ammonia solid III. At a constant pressure, the orientational disorder in ammonia solid III decreases as the temperature increases near the melting point (Fig. 1). The orientational disorder contributes to instability of the ammonia solid III, which causes anomalies in the specific heat  $C_P$ , thermal expansion  $\alpha_p$  and the isothermal compressibility  $\kappa_T$  prior to melting in this crystalline system.

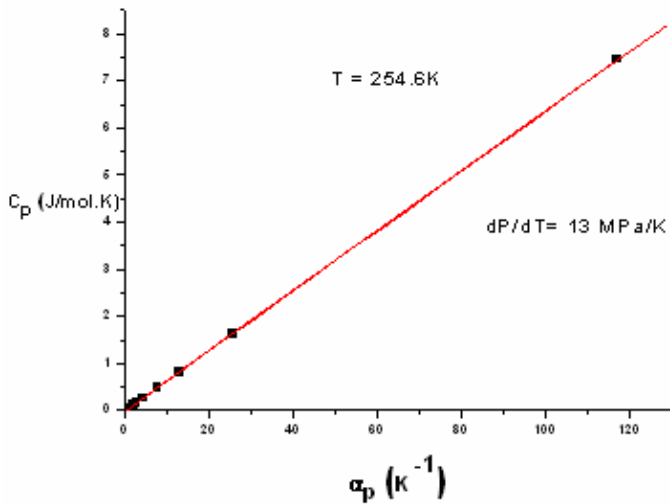
From linear variation of the specific heat  $C_P$  with the thermal expansion  $\alpha_p$ , variation of  $C_P$  with the pressure can be calculated according to the thermodynamic relation

$$\partial C_P / \partial P = VT(\alpha_p^2 + \partial \alpha_p / \partial T) \quad (21)$$

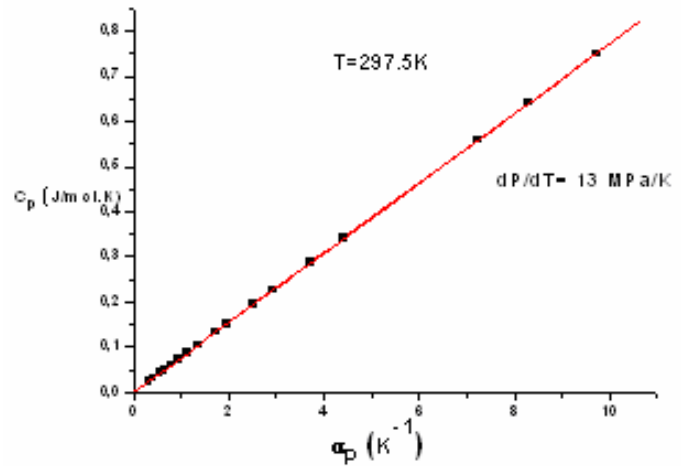
for ammonia solid III. This can also examine the critical behaviour of  $C_P$  and  $\alpha_p$  close to the melting point in ammonia solid III.

**Tab. 1.** Values of the critical exponent  $\gamma$  for the isothermal compressibility  $\kappa_T$  and the amplitude  $k$  from the analysis of the experimental data [16] according to Eq. (2) and the values of the intercept  $(dS/dT)_m$  extracted from Eq. (20) at the melting point for fixed temperatures indicated in the pressure range close to the melting point in ammonia solid III. Uncertainties in  $\gamma$  and  $\ln k$  are also given here.

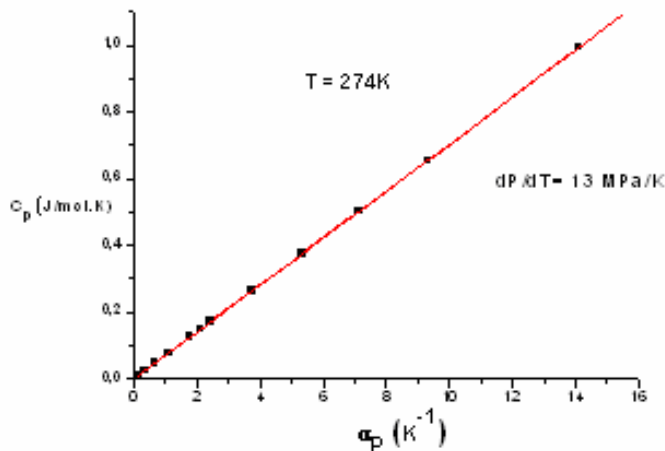
$T(K)$	$\gamma$	$\ln k$	$P - P_m(MPa)$	$(dS/dT)_m$ ( $J/mol.K^2$ )
254.6	$0.61 \pm 0.02$	$1.44 \pm 0.09$	$4.9 < P - P_m < 114.3$	$2.47 \times 10^{-2}$
274.0	$0.42 \pm 0.03$	$0.53 \pm 0.11$	$1.1 < P - P_m < 132.9$	$-3.65 \times 10^{-4}$
297.5	$0.46 \pm 0.05$	$0.70 \pm 0.18$	$1.7 < P - P_m < 146.5$	$-2.0 \times 10^{-2}$



**Fig. 5.** The specific heat  $C_p$  as a function of thermal expansion  $\alpha_p$  for 254.6K, according to Eq. (20) close to the melting pressure  $P_m$  in ammonia solid III.



**Fig. 7.** The specific heat  $C_p$  as a function of thermal expansion  $\alpha_p$  for 297.5K, according to Eq. (20) close to the melting pressure  $P_m$  in ammonia solid III.



**Fig. 6.** The specific heat  $C_p$  as a function of thermal expansion  $\alpha_p$  for 274K, according to Eq. (20) close to the melting pressure  $P_m$  in ammonia solid III.

#### 4 Conclusions

The specific heat  $C_p$  was related to the thermal expansion  $\alpha_p$  close to the melting pressure for constant temperatures at 254.6, 274 and 297.5K in ammonia solid III. A linear variation of  $C_p$  with  $\alpha_p$  was obtained here by analyzing the experimental data for the isothermal compressibility  $\kappa_T$  near the melting point in this solid system. The exponent values deduced from the analysis of the  $\kappa_T$  indicate that ammonia solid III undergoes a second order phase transformation prior to melting, as suggested for the ammonia solids I and II, previously. Also, a linear variation of  $C_p$  with  $\alpha_p$  is an indicative of similar critical behaviour of both

thermodynamic quantities which can be examined by the experimental measurements close to the melting point in ammonia solid III.

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