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A linear variation of the thermal expansivity with the isothermal compressibility for ammonia solid III near the melting point

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Abstract−The thermal expansivity α_p is related to isothermal compressibility κ_T at various pressures for constant temperatures of 254.6, 274 and 297.5 K close to the melting pressure in ammonia solid III. By analyzing the experimental data for κ_T according to a power-law formula, a linear variation of α_p with the κ_T is established here close to the solid-liquid transition in ammonia. Anomalous behavior of thermal expansivity α_p and the isothermal compressibility κ_T near the melting pressure is indicative of the λ-type transition in ammonia solid III.

Key words: Thermal Expansivity, Isothermal Compressibility, Melting Point, Ammonia Solid III

INTRODUCTION

Ammonia has been studied extensively since it melts at higher temperatures and pressures, as shown experimentally in its P-T [1-3] and V-T [4] phase diagrams. Melting curves of ammonia solid I (T_m=192.5 K, P=0) and solid II (T_m=222.4 K, P_m=3.07 kbar) have been calculated by using the mean field theory in our previous study [5]. We have also calculated a T-P phase diagram of ammonia including the solid phases I, II and III by the mean field theory [6].

Crystal structures of the solid phases of ammonia have been investigated by X-ray diffraction and neutron scattering techniques [7-9]. It has been reported [7,8] that the solid I has the cubic P_{213} structure with four molecules in the unit cell, whereas the solid II has a hexagonal-close-packed (hcp) structure with the space group $P6_3/mmc$ [9]. It has also been reported [2,9] that the solid III has the face centered cubic (fcc) with Fm3m between 240 and 300 K.

An experimental P-T phase diagram of ammonia has been obtained, as stated above, by recording the Raman spectra of the solid phases I, II and III of ammonia in the range of 214 to 280 K up to 870 MPa [3]. The Raman frequencies of the lattice modes of solid I, in particular, have been measured as a function of pressure at 214 K [3]. We have investigated the volume dependence of the Raman frequencies in ammonia solid I by calculating the Raman frequencies of the two translational and one librational mode for this crystalline system as a function of temperature near the melting point [10]. For ammonia solid II near the melting point, we have also calculated the Raman frequencies of a rotatory lattice mode as a function of pressure [11].

Prior to melting in ammonia, an experimental evidence has been given for a second order transformation by analyzing the isothermal compressibility κ_T measured at various pressures for fixed temperatures according to a power law formula [2,12]. By calculating the isothermal compressibility κ_T, thermal expansivity α_p and the specific heat C_P as a function of temperature close to the melting curves of solid I and II, we have indicated that ammonia exhibits a critical transition as one approaches the melting point in this system [13]. Regarding the divergence behavior of the thermodynamic quantities (κ_T, α_p and C_P) near the melting point in ammonia, we established the Pippard relations (a linear variation of C_P with α_p and also a linear variation of α_p with the κ_T) for ammonia solid I and II in our earlier study [14]. By relating the Raman frequency shifts (1/v) $(\partial v/\partial P)_T$ for a rotatory lattice mode to the thermal expansivity α_p, we have also modified the Pippard relation in ammonia solid II in the vicinity of the melting point [15].

In this study, we examine the Pippard relation (the thermal expansivity α_p against the isothermal compressibility κ_T), for ammonia III near the melting point by analyzing the experimental data for κ_T at various pressures for constant temperatures of 254.6, 274 and 297.5 K [12]. A linear variation of α_p with the κ_T is obtained for the three fixed temperatures considered in ammonia solid III. From the linear variations, the values of the slope dP_m/dT and the intercept $(dV/dT)_m$ are deduced.

In section 2, we give our calculations and results on the basis of the analysis of the experimental data [12] for ammonia solid III. Section 3 gives a discussion of our results. Conclusions are given in section 4.

CALCULATIONS AND RESULTS

The pressure dependence of the isothermal compressibility κ_T near the melting point can be described by a power-law formula [12]

$$\kappa_T = k(P - P_m)^{-\gamma} \tag{1}$$

where γ is the critical exponent, **k** is the amplitude of the isothermal compressibility and $\mathbf{P_m}$ is the melting pressure. Using the thermodynamic relation

$$\alpha_p/\kappa_T = dP_m/dT \tag{2}$$

near the melting point for ammonia solid III, the pressure dependence of the thermal expansivity α_p can be obtained from Eq. (1)

$$\alpha_p = k(dP_m/dT)(P - P_m)^{-\gamma} \tag{3}$$

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Table 1. Values of the critical exponent γ for the isothermal compressibility κ_T and the amplitude k from the analysis of the experimental data [12] according to Eq. (1) and the value of the intercept $(dV/dT)_m$ extracted from Eq. (7) at fixed temperatures indicated in the pressure range close the melting point in ammonia solid III. Uncertainties in γ and lnk are also given here

T(K)	γ	lnk	$P-P_m$ (MPa)	$-(dV/dT)_m$ (cm^3/mol·K)
254.6	0.61±0.02	1.44±0.09	$4.9<P-P_m<114.3$	55.51
274.0	0.42±0.03	0.53±0.11	$1.1<P-P_m<132.9$	55.31
297.5	0.46±0.05	0.70±0.18	$1.7<P-P_m<146.5$	47.71

Using the approximate relation,

$$[P-P_m(T)]/[T_m(P)-T]=dP_m/dT \quad (4)$$

close to the melting point for ammonia solid III, the temperature dependence of the isothermal compressibility κ_T and of the thermal expansivity α_p then become:

$$\kappa_T=k(dP_m/dT)^{-\gamma}(T_m-T)^{-\gamma} \quad (5)$$

and

$$\alpha_p=k(dP_m/dT)^{1-\gamma}(T_m-T)^{-\gamma} \quad (6)$$

respectively.

We can relate the thermal expansivity α_p to the isothermal compressibility κ_T near the melting point for ammonia solid III, and establish a linear variation of α_p with the κ_T according to the relation.

$$\alpha_p=(dP_m/dT)\kappa_T+(1/V)\,(dV/dT)_m \quad (7)$$

In Eq. (7) $(dV/dT)_m$ denotes the variation of the volume V with the temperature at the melting point for ammonia solid III.

We analyzed here the experimental data for the isothermal compressibility κ_T at various pressures for the fixed temperatures of 254.6, 274 and 297.5 K [12] near the melting point for ammonia solid III. This analysis was performed by using the power-law formula (Eq. (1)). Table 1 gives the values of the critical exponent γ for the κ_T and the amplitude k within the pressure ranges for the constant temperatures studied close to the melting point in ammonia solid III. Fig. 1 gives κ_T against $P-P_m$ in a log-log plot for a constant temperature of 254.5 K for ammonia solid III. Then we calculated the thermal expansivity α_p as a function of $P-P_m$ according to Eq. (3) using the values of γ and k for T=254.6 K near the melting point of ammonia solid III. In Eq. (3) we used the experimental values of dP_m/dT=13 MPa/K [12].

Similarly, we analyzed the experimental data for the isothermal compressibility κ_T at various pressures for the fixed temperatures of 274 and 297.5 K [12] according to Eq. (1) near the melting point in ammonia solid III. From our analysis, the values of the critical exponent gamma and the amplitude k for the temperatures of 274 and 297.5 K are tabulated within the pressure ranges considered in Table 1. In a log-log plot we give κ_T as function of $P-P_m$ for 274 K in Fig. 2. Using Eq. (3), the α_p values were evaluated at various pressures for 274 K with the values of γ and k (Table 1).

Finally, by analyzing the experimental data for the isothermal compressibility κ_T as a function of pressure for a fixed temperature of 297.5 K [12] as plotted in Fig. 3, we extracted the values of γ and k within the pressure range (Table 1). We then evaluated the thermal expansivity α_p as a function of $P-P_m$ according to Eq. (3) for 297.5 K.

Since we started by analyzing the experimental data for the isothermal compressibility κ_T and then we calculated the thermal expansivity α_p using Eq. (3) at various pressures for constant temperatures

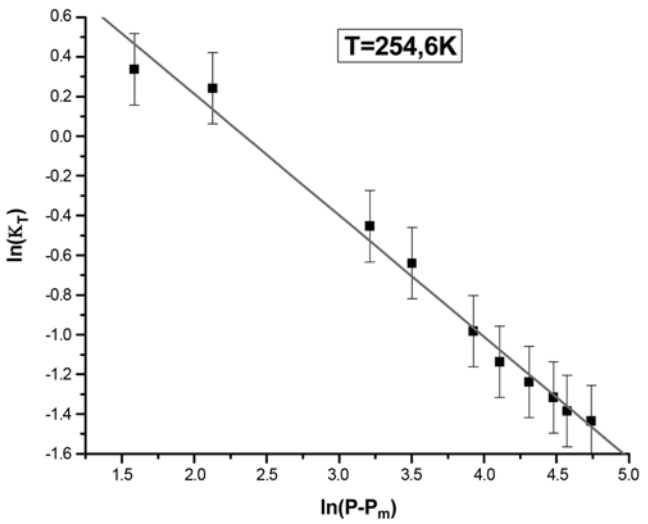

Fig. 1. A log-log plot of the isothermal compressibility κ_T as a function of $P-P_m$ for 254.6 K from the analysis of the experimental data [12] according to Eq. (1) close to the melting pressure P_m in ammonia solid III. Uncertainties in κ_T are also indicated here.

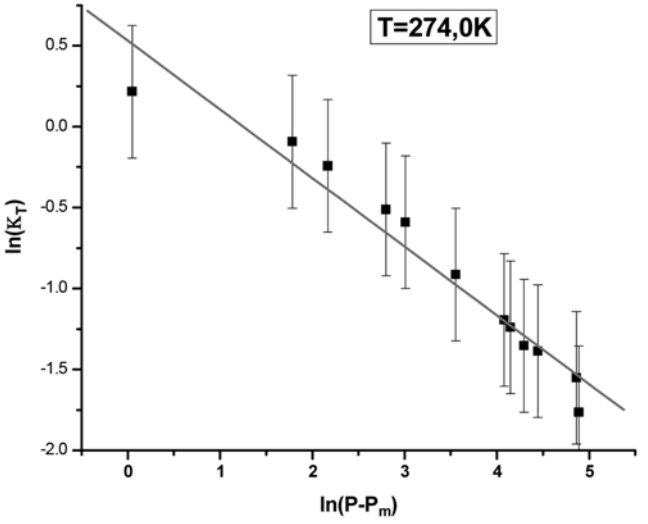

Fig. 2. A log-log plot of the isothermal compressibility κ_T as a function of $P-P_m$ for 274 K from the analysis of the experimental data [12] according to Eq. (1) close to the melting pressure P_m in ammonia solid III. Uncertainties in κ_T are also indicated here.

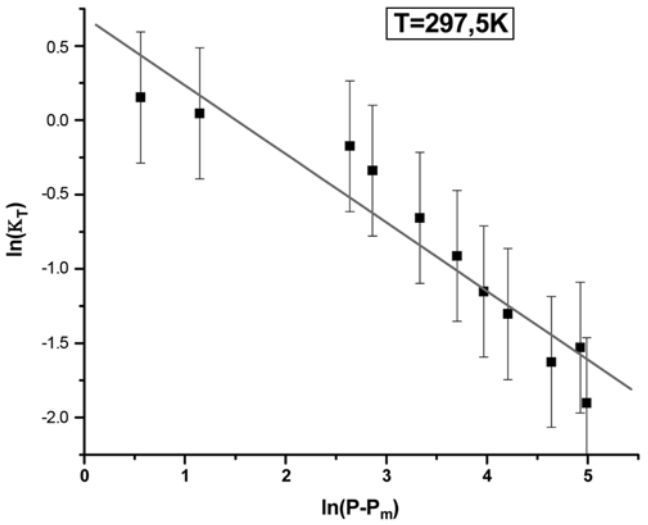

Fig. 3. A log-log plot of the isothermal compressibility κ_T as a function of P−P_m for 297.5 K from the analysis of the experimental data [12] according to Eq. (1) close to the melting pressure P_m in ammonia solid III. Uncertainties in κ_T are also indicated here.

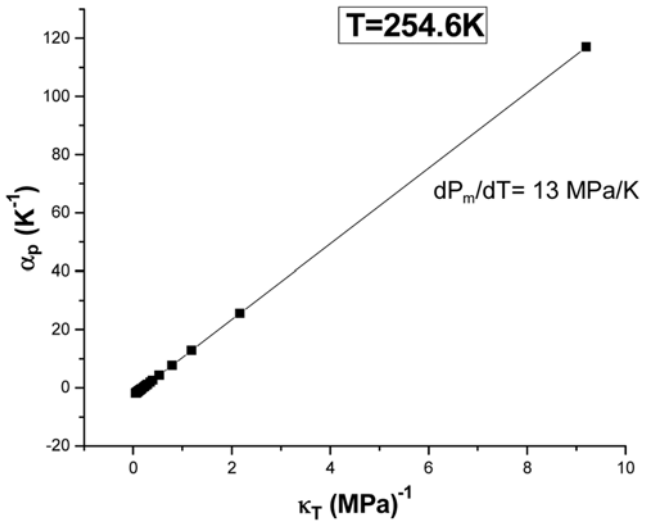

Fig. 4. The thermal expansivity α_p as a function of the isothermal compressibility κ_T for 254.6 K, according to Eq. (7) close to the melting pressure P_m in ammonia solid III.

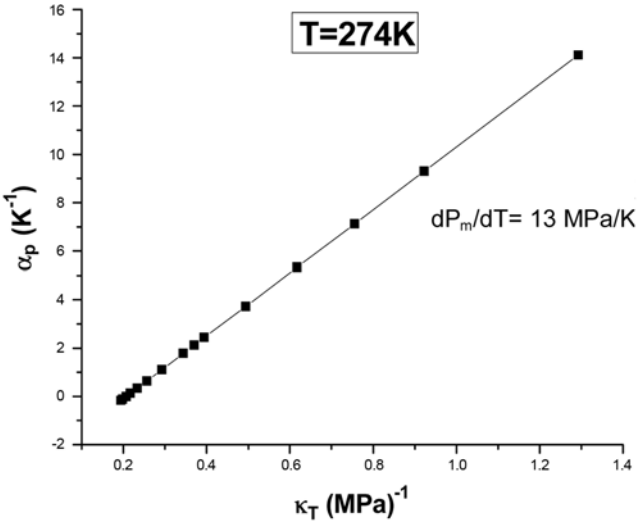

Fig. 5. The thermal expansivity α_p as a function of the isothermal compressibility κ_T for 274 K according to Eq. (7) close to the melting pressure P_m in ammonia solid III.

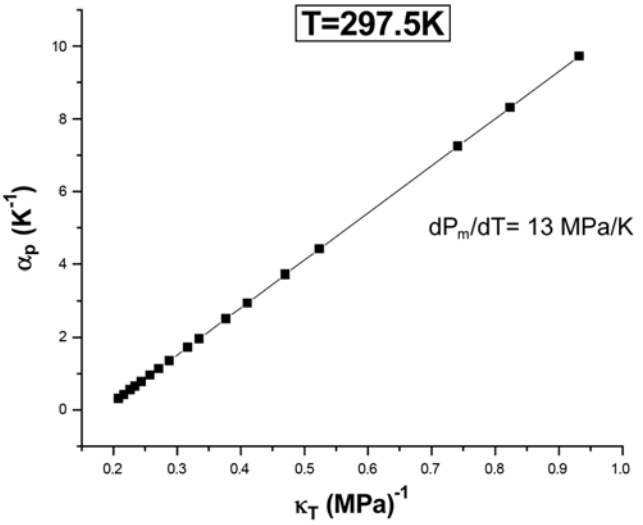

Fig. 6. The thermal expansivity α_p as a function of the isothermal compressibility κ_T for 297.5 K according to Eq. (7) close to the melting pressure P_m in ammonia solid III.

of 254.6, 274 and 297.5 K for ammonia solid III, we were able to obtain the Pippard relation of α_p against κ_T. Figs. (4-6) give our plots of α_p versus κ_T for the temperatures of 254.6, 274 and 297.5 K, respectively, according to Eq. (7) near the melting point for ammonia solid III. From our plots, (Figs. 4-6), we extracted the values of the intercept $(dV/dT)_m$ for constant temperatures of 254.6, 274 and 297.5 K, respectively, as given in Table 1.

DISCUSSION

Our calculations for the thermal expansivity α_p and the isothermal compressibility κ_T at various pressures showed that they varied linearly for constant temperatures of 254.6, 274 and 297.5 K, as given in Figs. (4-6), respectively. This indicates that the thermal expansivity and the isothermal compressibility exhibit similar critical behavior close to the melting point in ammonia solid III. This critical behavior is almost the same regarding the γ values (Table 1) for constant temperatures of 274 K (Fig. 5) and 297.5 K (Fig. 6) with the same slope of 13 MPa/K obtained experimentally [12]. On the other hand, the variation of the molar volume with the temperature has the same values of $dV/dT = -55$ cm^3/ mol·K for constant temperatures of 254.6 K (Fig. 4) and 274 K (Fig. 5). Although there are experimental uncertainties in the isothermal compressibility κ_T measured as a function of P−P_m, as shown in Figs. (1-3), the same uncertainties should also occur in the thermal expansivity α_p. With those uncertainties in the κ_T and α_p when they are plotted for

the same pressures in the pressure interval (Table 1) close to the melting point, they vary linearly, as given in Figs. (4-6) for constant temperatures of 254.6, 274 and 297.5 K, respectively, in ammonia solid III. This linear variation of α_p with the κ_T which follow power laws (Eqs. (1) and (3) or Eqs. (5) and (6)), indicates that the ammonia solid III exhibit a λ-type transition, as suggested for ammonia solids previously [16].

Since a λ-type transition is regarded as a second-order phase transformation, ammonia solid III exhibits this transformation prior to melting [12]. A second-order transition that occurs in ammonia solid III may be due to reorientation of NH_3 molecules, which is an orientational disorder [16]. In the temperature or pressure range where the orientational disorder occurs, the thermal expansivity α_p and the isothermal compressibility κ_T exhibit anomalous behavior in ammonia solid III.

From the linear variation of the thermal expansivity α_p with the isothermal compressibility κ_T (Figs. 4-6), one can determine the change in enthalpy ΔH by knowing the change in the molar volume ΔV for ammonia solid III according to Clapeyron equation

$$dP_m/dT=\Delta H/T_m \cdot \Delta V \quad (8)$$

where $\Delta H=H-H_m$ and $\Delta V=V_s-V_m$. Here H_m and V_m denote the enthalpy and the molar volume (solid volume V_s) at the melting point. ΔH can be calculated for the three constant temperatures (T_m= 254.6, 274 and 297.5 K) in ammonia solid III.

CONCLUSIONS

A linear variation of the thermal expansivity α_p with the isothermal compressibility κ_T was obtained in this study near the melting point in ammonia solid III. α_p and κ_T were calculated by using the values of the critical exponent γ and the amplitude k, which we determined from the analysis of the experimental data for the pressure dependence of the isothermal compressibility close to the melting point in ammonia solid III. It was shown here that a power-law formula can be approximately used to predict a linear variation of the thermal expansivity with the isothermal compressibility near the melting point in ammonia solid III. By the experimental measurements for α_p and κ_T, our predictions given here can be examined for this solid system near the melting point.

REFERENCES

1. R. C. Hanson and M. J. Jordan, *J. Phys. Chem*., **84**, 1173 (1980).
2. R. L. Mills, D. H. Liebenberg and Ph. Pruzan, *J. Phys. Chem*., **86**, 5219 (1982).
3. M. Gauthier, Ph. Pruzan, J. M. Besson, G. Havel and G. Syfosse, *Physica*, **139&140 B**, 218 (1984).
4. C. L. Nye and F. D. Medina, *Phys. Rev. B*, **32**, 2510 (1985).
5. S. Salihoğlu, Ö. Tar and H. Yurtseven, *Phase Trans*., **72**, 299 (2000).
6. Y. Enginer, S. Salihoğlu and H. Yurtseven, *Mater. Chem. and Phys*., **73**, 57 (2002).
7. I. Olovsson and D. H. Templeton, *Acta Crystallogr*., **12**, 832 (1959).
8. J. W. Reed and P. M. Harris, *J. Chem. Phys*., **35**, 1730 (1961).
9. J. Eckert, R. L. Mills and S. Satija, *J. Chem. Phys*., **81**, 6034 (1984).
10. H. Yurtseven, *J. Phys. Chem. A*, **103**, 5900 (1999).
11. H. Yurtseven, *Chin. J. Phys*., **42**, 209 (2004).
12. Ph. Pruzan, D. H. Liebenberg and R. L. Mills, *J. Phys. Chem. Solids*, **47**, 949 (1986).
13. H. Yurtseven and S. Salihoğlu, *Chin. J. Phys*., **40**, 416 (2002).
14. H. Yurtseven, *Int. J. Mod. Phys. B*, **13**, 2783 (1999).
15. H. Karaçalı and H. Yurtseven, *J. Chem. Sci*., **117**, 677 (2005).
16. Ph. Pruzan, D. H. Liebenberg and R. L. Mills, *Phys. Rev. Lett*., **18**, 1200 (1982).