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Analysis of The Molar Volume as A Function of Pressure Close to The Melting Point in Ammonia Solid III

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This study gives the calculation of the molar volume as a function of pressure for constant temperatures in ammonia solid III near the melting point. Using the value of the critical exponent γ extracted from the experimental data for the isothermal compressibility κ_T. The molar volume calculated here decreases as the pressure increases on approach to the melting point. This critical behaviour can describe the observed behaviour of the molar volume near the melting point, as obtained experimentally in ammonia solid III.

Key Words: Molar volume, Melting point, Ammonia solid III.

INTRODUCTION

Solid phases of ammonia are interesting to study since they melt at higher temperatures and pressures. Ammonia solid I melts at $T_m = 192.5$ K at atmospheric pressure. At a higher pressure of 3.07 kbar, ammonia solid II melts at $T_m = 222.4$ K. At a very high pressure of 35 kbar at 25 ºC, the solid II transforms into the solid III phase in ammonia, as obtained experimentally[1]. The solid I, II and III phases of ammonia have been obtained experimentally in P-T[1-3] and V-T[4] phase diagrams. The melting curves of the solid I and II phases[5] and also the phase curves of the solid I, II and III phases have been calculated using the mean field theory in earlier studies[6].

Regarding the crystal structures of the solid phases in ammonia, X-ray diffraction[7] and neutron scattering[8] techniques have determined the solid I phase which has the cubic $P_{2,3}$ structure, whereas the solid II phase has a hexagonal-close packed (hcp) structure that has the space group $P6_3/mmc$[9]. It has also been determined experimentally that the solid III phase has the face centered cubic (fcc) with Fm3m[4,9].

Volume dependence of the Raman frequencies in ammonia solid I, which measures anharmonicity in this crystal has been studied experimentally by determining the mode Gruneisen parameters of the two translational and one librational mode[4]. For ammonia solid II, the temperature and volume dependences of the translational and vibrational modes have been studied experimentally[10].

Raman frequencies of the translational mode as a function of temperature[11] and pressure[12] in ammonia solid II are calculated. Raman frequency shifts for translational modes[13] and the rotatory lattice mode[14] close to the melting point in ammonia solid I are also calculated. In recent studies, Raman frequency shifts for the rotatory mode[15] and the translational modes[16] were related to specific heat of the ammonia solid I. For ammonia solid II, Raman frequency shifts of the translational mode has been related to the thermal expansivity near the melting point in recent study[17].

Molar volume of ammonia solid I, II and III has been measured as a function of pressure at constant temperatures near the melting point[18]. The molar volume of ammonia solid III, in particular, which we study here has been measured as a function of pressure for constant temperatures of 263.4 and 297.5 K[18].

In this study, the molar volume is calculated using the expression derived from the divergence behaviour of the isothermal compressibility κ_T as a function of pressure close to the melting point in ammonia solid III[18]. The values of the critical exponent γ for the isothermal compressibility κ_T are determined from the analysis of the experimental data[18] for the molar volume of ammonia solid III close to the melting pressure.

RESULTS AND DISCUSSION

Close to the melting point of ammonia solid III, the pressure dependence of the isothermal compressibility κ_T can be described by a power-law formula[18],

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

where γ is the critical exponent for the isothermal compressibility, k is the amplitude and P_m is the melting pressure which is assumed to be close to the critical pressure for ammonia solid III. By using the definition of the isothermal compressibility,

$$\kappa_T \equiv -(1/V)\,(\partial V/\partial P)_T \tag{2}$$

the pressure dependence of the volume can be obtained as

$$V(P) = V_c \exp\,[-k(1-\gamma)^{-1}(P- P_m)^{-1-\gamma}] \tag{3}$$

The temperature dependence of the volume can also be obtained by writing the variation of the melting pressure P_m with the temperature as an approximate relation[18],

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

By using eqn. 4 in eqn. 3, one gets the volume as a function of temperature as

$$V(T) = V_c \exp\,[-k(1-\gamma)^{-1}\,(dP_m/dT)^{1-\gamma}\,(T_m-T)^{1-\gamma}] \tag{5}$$

We analyzed here the pressure dependence of the volume of the ammonia solid III for the fixed temperatures of 263.4 and 297.5 K, according to eqn. 3 using the experimental data[18]. From our analysis of the volume data at various pressures[18], we determined the values of the critical exponent γ and the coefficient k by taking the logarithm of both sides of eqn. 3, which gives

$$\ln V\,(P) = \ln V_c - k(P-P_m)^{-1-\gamma}/(1-\gamma) \tag{6}$$

By using the observed values of the volume for T = 263.4 K[18], we obtained the values of γ and k, as given in Table-1. We also determined the values of γ and k for the fixed temperature of 297.5 K by using the observed values of the volume[18] according to eqn. 6, as tabulated in Table-1. Figs. 1 and 2 give the plots of the volume V as a function of pressure P for the temperatures of 263.4 and 297.5 K, respectively. According to eqn. 3 where the volume values were calculated using the γ and k values (Table-1) within the pressure intervals indicated.

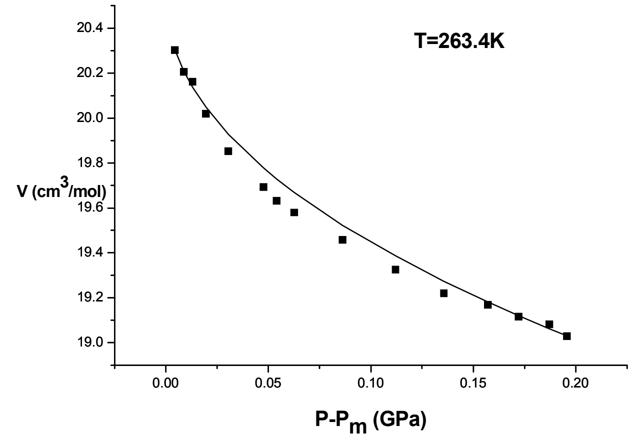

Fig. 1. Molar volume V calculated (solid curve) as a function of P-P$_m$ for 263.4 K according to eqn. 3 close to the melting pressure P$_m$ in ammonia solid III. Experimental data points[18] are shown here

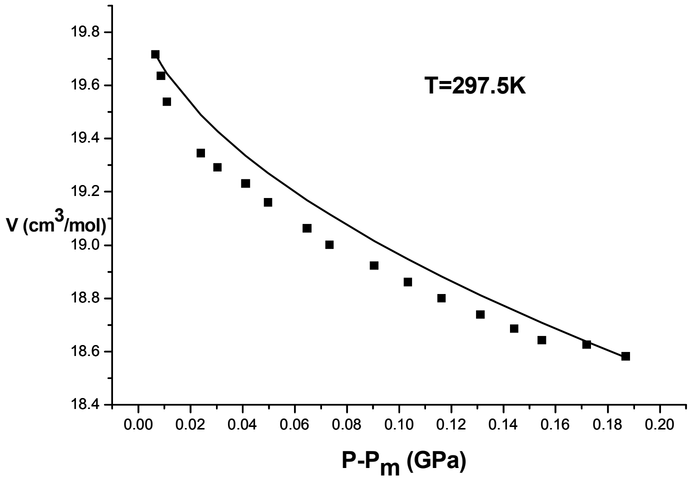

Fig. 2. Molar volume V calculated (solid curve) as a function of P-P$_m$ for 297.5 K according to eqn. 3 close to the melting pressure P$_m$ in ammonia solid III. Experimental data points[18] are shown here

TABLE-1
VALUES OF THE CRITICAL EXPONENT γ FOR THE ISOTHERMAL COMPRESSIBILITY κ_T AND THE AMPLITUDE K OBTAINED ACCORDING TO eqn. 6 FOR THE TEMPERATURES INDICATED NEAR THE MELTING POINT IN AMMONIA SOLID III AND THE EXPERIMENTAL VALUES OF THE MELTING PRESSURE P$_m$ AND THE CRITICAL VOLUME V$_c$

T (K)	P$_m$ (GPa)	V$_C$ (cm^3/mol)	γ	k (GPa$^{\gamma-1}$)
263.4	0.67	20.54	0.50	0.086
297.5	0.99	19.94	0.45	0.098

The molar volume decreases as the pressure increases close to the melting pressure for constant temperatures of 263.4 and 297.5 K, as shown in Figs. 1 and 2, respectively. This is the critical behaviour expected for the molar volume as the melting point is approached. Similar critical behaviour of the molar volume for both constant temperatures (Figs. 1 and 2) is accompanied with the values of critical exponent γ for the isothermal compressibility, which are close to each other (Table-1). Present exponent value of $\gamma \cong 0.5$ is completely different from the mean field value ($\gamma = 1$) and also the values expected from the theoretical models ($\gamma > 1$). From the analysis of the experimental data for the isothermal compressibility κ_T at various pressures, values of the critical exponent have been obtained as $\gamma = 0.49$ and 0.60 for the ammonia solids I and II, respectively[19]. These exponent values have been extracted for constant temperatures in ammonia solids I and II[19]. It has been pointed out that two different values of the critical exponent γ could result differences in the two crystal structures for the ammonia solids I and II[19]. In comparison with present exponent value of $\gamma \cong 0.5$ for both constant temperatures in ammonia solid III (Table-1), this may also indicate that the solid III has similar structure as the solid I. This is in fact the case that both solids I and III have cubic structures (solid I has the simple cubic and solid III has the face-centered cubic), whereas solid II is the hexagonal closed packed, as determined by X-ray diffraction[7,9]. The exponent value for ammonia solids I and III is equal to the value of 0.5 calculated for the thermal expansivity α_p[20] in alkali halides using quasiharmonic theory, as also pointed out previously[19].

The exponent value of $\gamma = 0.5$ for the isothermal compressibility κ_T of ammonia solids I and III, is an indicative that the ammonia solids undergo a second order phase transformation prior to melting, as pointed out previously[18].

As shown in Figs. 1 and 2, the calculated curves for the molar volume are not in good agreement with the experimental data points[18]. This discrepancy may be due to the fact that we calculated the molar volumes on the assumption that the critical pressure is equal to the melting pressure, as also indicated previously[18]. So, the critical volume V_C should be between the solid volume $V_{s,m}$ and the liquid volume $V_{l,m}$ close to the melting point[19]. Also, the pressure dependence of the isothermal compressibility κ_T as a power-law formula (eqn. 1) is approximate to describe the critical behaviour near the melting point in ammonia solid III. It has been reported[18] that there is a lack of accurate thermodynamic data in the melting zone and in the solid phase. This may also cause the discrepancy between currently calculated and observed molar volumes.

Conclusion

The molar volume of ammonia solid III was calculated here as a function of pressure for constant temperatures of 263.4 and 297.5 K close to the melting pressure. This calculation was performed by analyzing the experimental data for the isothermal compressibility at various pressures for constant temperatures indicated according to a power-law formula.

Present calculated molar volumes provided the critical behaviour for both constant temperatures, which agreed mostly with the experimental data. It is suggested here that a power-law formula which describes the critical behaviour can be used as an approximate relation close to the melting point to predict the observed behaviour of the molar volume for ammonia solid III, as given in this study.

REFERENCES

1. R.L. Mills, D.H. Liebenberg and Ph. Pruzan, *J. Phys. Chem.*, **86**, 5219 (1982).
2. R.C. Hanson and M. Jordan, *J. Phys. Chem.*, **84**, 1173 (1980).
3. M. Gauthier, Ph. Pruzan, J.M. Besson, G. Havel and G. Syfosse, *Physica*, **139-140B**, 218 (1986).
4. C.L. Nye and F.D. Medina, *Phys. Rev.*, **32**, 2510 (1985).
5. S. Salihoglu, Ö. Tari and H. Yurtseven, *Phase Trans.*, **72**, 299 (2000).
6. Y. Enginer, S. Salihoglu and H. Yurtseven, *Mater. Chem. 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. R.K. Luo and F.D. Medina, *Phys. Rev. B*, **42**, 3190 (1990).
11. H. Yurtseven, *Spectrochim. Acta A*, **59**, 1003 (2003).
12. H. Yurtseven, *J. Quant. Spect. Rad. Trans.*, **102**, 409 (2006).
13. H. Yurtseven and H. Karaçali, *Phil. Mag.*, **85**, 2913 (2005).
14. H. Karaçali and H. Yurtseven, *J. Phys. Chem. B*, **109**, 16974 (2005).
15. H. Karaçali and H. Yurtseven, *J. Quant. Spect. Rad. Trans.*, **98**, 57 (2006).
16. H. Yurtseven and H. Karaçali, *Spectrochim. Acta*, **67A**, 1060 (2007).
17. H. Yurtseven and H. Karaçali, *Spectrochim. Acta*, **68A**, 802 (2007).
18. Ph. Pruzan, D.H. Liebenberg and R.L. Mills, *J. Phys. Chem. Solids*, **47**, 949 (1986).
19. Ph. Pruzan, D.H. Liebenberg and R.L. Mills, *Phys. Rev. Lett.*, **48**, 1200 (1982).
20. L.L. Boyer, *Phys. Rev.*, **B23**, 3673 (1981).

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