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Temperature and pressure dependence of molar volume in solid phases of ammonia near the melting point

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Temperature and pressure dependencies of the molar volume are studied here along the transition curve between solid I and solid II phases near the melting point in ammonia. The molar volumes are calculated in the temperature range of 217 to 224 K and in the pressure range of 3 to 8 kbar with respect to the triple point (T_t=217.34 K, P_t=3.070 kbar) where the melting curves of solid I and solid II coincide with the transition curve in ammonia.

1. Introduction

Ammonia has been studied extensively in the literature since it exhibits critical behaviour close to the melting point. Although many studies have concentrated on melting of the solid phases in ammonia, it is of interest to study the critical behaviour among the solid phases near the melting point in this system.

Solid ammonia has three solid phases, namely, solid I, solid II [1] and solid III [2]. At a higher pressure of 4 GPa, another solid phase IV occurs [3]. This phase has been found stable in the neutron diffraction experiments up to 9 GPa [4,5]. From an X-ray study at higher pressures up to 123 GPa [3], phase V and from the Raman study at high pressures up to 60 GPa [6], a possible phase VI of solid ammonia have been suggested. At the melting temperature of T_m = 192.5 K at atmospheric pressure, there occurs a phase transition from solid I to the liquid phase. At the pressures above 3 kbar and temperatures above 220 K, the solid II phase melts. As we increase the pressure, solid I phase transforms into the solid II phase. It has been indicated that the solid II phase transforms into the solid III phase between the temperatures of 240 and 300 K [7, 8]. The phase lines between solid I–liquid, solid II–liquid and solid I–solid II meet at the triple point of T_{L-I-II} = 217.34 K (P = 3.070 kbar). There is also another triple point among the gaseous, liquid, and solid I phases, which is located at T_{G-L-I} = 195.48 K (P = 0 kbar). All those phases have been shown in the experimental P–T [1,7,9] and V–T [10] phase diagrams in ammonia as also given in Fig. 1 [7]. By using the mean field theory, we have obtained a P–T phase diagram which contains solid I, solid II and liquid phases [11], and a P–T phase diagram of ammonia solids I, II and III [12].

The crystal structures of solid ammonia have been determined experimentally. Ammonia solid I has a simple cubic structure [13–15] containing four molecules per unit cell with the space group P_{213}. Ammonia solid II has a hexagonal-close-packed structure which contains two orientationally disordered molecules per unit cell with the space group $P6_3/mmc$ [8]. Ammonia solid III phase that has been discovered experimentally at room temperature (25 °C) and at a high pressure (35 kbar), has a face centered cubic structure [7] with the space group $Fm\bar{3}m$[2]. The crystal structure of phase IV has been determined as hexagonal-close-packed (hcp) by X-ray diffraction [16] previously. But neutron diffraction on ND_3 has revealed an orthorhombic structure with space group $P2_12_12_1$, which has rotationally ordered molecules [4,5], as also pointed out previously [3]. More recently, it has been suggested that phase IV has a monoclinic structure by X-ray study up to 40 GPa [17]. X-ray experiments up to 123 GPa show that solid IV has the orthorhombic symmetry [3]. Phase V and possible phase VI are different from phase IV because of the arrangements of the hydrogen atoms, as suggested previously [3]. For phase VI, cubic structures have been proposed on the basis of the Raman experiments [6].

Apart from the experimental techniques such as the X-ray [13] and neutron scattering [14], which have been applied to ammonia solids I and solid II, the Raman measurements have been taken, in particular, for solid I [9,10] and solid II [9,18,19] in ammonia. Also, experimental studies on phase III [2] and using Raman [6], Brillouin [20] and X-ray diffraction techniques on phase IV have been reported in earlier studies.

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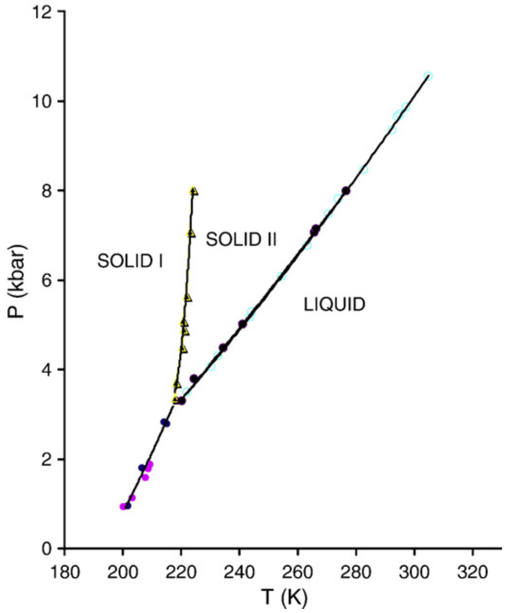

Fig. 1. Experimental P–T phase diagram of ammonia: Solid lines represent melting curves and transition lines I–II [7].

It has been pointed out in the works of Pruzan et al. [21,22] that the solid ammonia exhibits the critical behaviour near the melting point. In their studies, they have described the critical behaviour of the isothermal compressibility and the thermal expansivity in ammonia by means a power-law formula since the transition is of a second order type prior to melting [21,22]. We have calculated [23] the critical behaviour of the isothermal compressibility, thermal expansivity and the specific heat for solid ammonia on the basis of the experimental data of Pruzan et al. [21]. We have also applied the Pippard relations relating those thermodynamic quantities, namely, the specific heat to the thermal expansivity and thermal expansivity to the isothermal compressibility for the ammonia system near the melting point [24]. In our recent studies, we have examined the critical behaviour of ammonia solid I [25] and solid II [26] by means of the Raman frequency shifts near the melting point.

In this study, we calculate the temperature and pressure dependence of the molar volume of solid ammonia along the transition curve between solid I and solid II phases. Our calculations for the temperature and pressure dependencies of the molar volume in the solid I and II phases of ammonia, are based on the experimental analysis for this system due to Pruzan et al. [21]. The volume calculations performed here at the transition and the triple point according to the power-law formula of Pruzan et al. [21], are approximations since these power-law formulae are valid close to the melting temperature for the solids I and II in ammonia. By predicting the temperature and pressure dependencies of the molar volume for the ammonia solids I and II, it is aimed here to give a theoretical basis for a second order transformation prior to melting in ammonia, as given an experimental evidence by Pruzan et al. [22].

Below, in Section 2 we give our calculations and results. We discuss our results in Section 3. Finally, conclusions are given in Section 4.

2. Calculations and results

Near the melting point of solid ammonia, the critical behaviour of the thermodynamic functions can be described by a power-law formula. For example, the volume values can be obtained from the pressure dependence of the isothermal compressibility $\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ according to the power-law formula

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

where $\gamma^* = \gamma/(2-\alpha)$. In this relation γ is the critical exponent for the isothermal compressibility, which is equal to 1.24 (nonclassical theory) and 1 for classical theory. α is the critical exponent for the isochoric heat capacity and k is the amplitude. Thus, Eq. (1) can describe the critical behaviour of the isothermal compressibility κ_T of ammonia solids I and II near the melting point. This power-law formula gives directly the solid volume V_S at pressure differing from the melting pressure P_m at the same temperature as

$$V_s = V_c \exp\left[-k\left(1-\gamma^*\right)^{-1}(P-P_m)^{1-\gamma^*}\right] \tag{2}$$

where V_c is the critical volume which is determined by the melting temperature.

The temperature dependence of the crystal volume can also be obtained for the ammonia solid near the melting point by regarding the ratio [22] given below:

$$\frac{P - P_m(T)}{T_m(P) - T} = \frac{dP_m}{dT_m} \tag{3}$$

By inserting Eq. (3) into Eq. (2), we get the volume of a single-phase solid (I or II) at temperature differing from the melting temperature T_m at the same pressure as

$$V_s = V_c \exp\left[-k\left(1-\gamma^*\right)^{-1}\left(\frac{dP_m}{dT_m}\right)^{1-\gamma^*}(T_m-T)^{1-\gamma^*}\right] \tag{4}$$

close to the melting point in ammonia. Here, the critical volume V_c is the molar volume, as in Eq. (2), at the melting point (P_m,T_m), which is defined in the solid I and II phases of ammonia for its solid–liquid phase transition. In Eqs. (2) and (4), the critical volume for the ammonia solids I and II can be expressed empirically as,

$$V_c(I) = V_I - d_I(T_m - T_t) \tag{5}$$

and

$$V_c(II) = V_{II} - d_{II}(T_m - T_t) \tag{6}$$

respectively [21]. In Eqs. (5) and (6) V_I and V_{II} are constant values of molar volume V_c for solid I and II phases, respectively, when the melting temperature T_m is at the triple points between gaseous, liquid and solid I phases ($T_t = T_{G-L-I} = 195.48$ K, $P = 0$ kbar) and between liquid, solid I and II phases ($T_m = T_{L-I-II} = 217.34$ K, $P = 3.070$ kbar). d_I and d_{II} represent negative volume change per unit change in temperature for the solid I and II phases, respectively.

2.1. Calculation of molar volume as a function of pressure

We first calculated here the pressure dependence of the molar volume of ammonia along the phase line between solid I and solid II. This was done by means of Eq. (2) for the solid I and II phases in ammonia using the experimental values due to Pruzan et al. [21]. Those experimental values were obtained from their analysis for the pressure dependence of the isothermal compressibility κ_T according to Eq. (1) along the melting curves of solids I and II in ammonia [21].

Along the melting curves of solids I and II, the temperature dependence of the pressure, $P_m(I)$ and $P_m(II)$, was given by Pruzan et al.[21] as empirical relations. Since the melting curves of solid I and solid II coincide at the triple point with the coordinates $T_t = 217.34$ K,