



CALCULATION OF THE PHASE DIAGRAMS FOR THE FLUID-SOLID AND SOLID-SOLID (δ - δ_{loc} - ϵ) TRANSITIONS IN MOLECULAR NITROGEN BY USING MEAN FIELD MODEL

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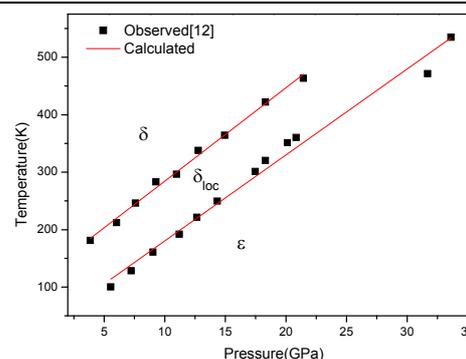
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The temperature-pressure (T-P) phase diagrams are calculated using the mean field models for the solid-fluid (first order) and, the solid-solid transitions of the δ - δ_{loc} (second order) and δ_{loc} - ϵ (first order) in nitrogen. By expanding the free energy in terms of the order parameters, the phase line equations are derived and they are fitted to the experimental data from the literature for this molecular crystal. For the fitting procedure, the coefficients in the free energy expansion are assumed to be the temperature and pressure dependent.

The mean field models presented here can explain the observed T-P phase diagram of nitrogen. The critical behavior of some thermodynamics quantities can also be predicted by the mean field models close to the solid-fluid and solid-solid transitions in this molecular crystal.



INTRODUCTION

Solid molecular nitrogen at high pressures can transform into an atomic solid with a single-bonded crystalline structure.¹ Its single-bonded cubic form has been studied experimentally at temperatures above 2000K and pressures above 110GPa.² At ambient conditions, nitrogen exists in atomic molecular form with very strong N≡N triple bonds³ and there occur fundamental pressure- and temperature- induced phase changes in this molecular crystal.

Phase diagrams including various phases of N₂ have been obtained spectroscopically by Raman scattering and X-ray diffraction, namely, the phases of α -N₂,^{4,5} β -N₂,^{5,6} γ -N₂,^{5,7} δ -N₂⁸ and ϵ -N₂.⁹ By Raman spectroscopy, the phase diagram for the

$\alpha, \beta, \gamma, \delta$ and fluid N₂ has been determined.¹⁰ T-P phase diagrams at high temperatures and pressures including θ, ζ and η phases¹¹ and, δ and δ_{loc} phases¹² in nitrogen have also been obtained experimentally. Very recently, we have calculated T-P phase diagram of nitrogen using the mean field theory.¹³ Regarding the liquid-solid transition in N₂, its high-pressure melting curve has been measured to 1400 K at 71 GPa [14] and also the T-P phase diagrams for the fluid-solid transition have been obtained experimentally.^{15,16}

At low pressures, a number of partially disordered structures are known where the N₂ molecules freely rotate in spheres or disks.^{7,9} An experimental study of the phase transitions at high temperatures in compressed solid nitrogen has been performed using Raman spectroscopy regarding the transition between the disordered δ

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and δ_{loc} phases and the ordered ε phase.¹² The δ phase is disordered with the molecules orientationally distributed between corners and faces of a fcc unit cell.¹¹ With the ordered rhombohedral structure,¹⁷ ε -N₂ occurs at around 16 GPa at room temperature, which becomes stable in this pressure and temperature range^{9,18,19} as evidenced by the Brillouin scattering²⁰ and x-ray diffraction studies.^{18,19} At pressures higher than 20 GPa, calculations indicate that a phase transition occurs from the cubic Pm3n phase into a tetragonal phase with 32 molecules per primitive cell.²¹ In our earlier studies, the mechanism of phase transitions has also been investigated in nitrogen by calculating the Raman frequencies of various modes in different phases of this crystal.²²⁻²⁵

In this study, the temperature-pressure (T-P) phase diagram of molecular nitrogen is calculated for the fluid-solid transition and also for the transitions of the δ - δ_{loc} and δ_{loc} - ε (solid-solid transitions) by using the mean fields models. For the first order fluid-solid transition¹⁶ and calculation of the melting temperatures at higher pressures up to 71 GPa¹⁴ in nitrogen, the mean field model is used with the free energy expanded in terms of the order parameter with the cubic term. For the second order transition of the δ - δ_{loc} in N₂,¹² the free energy expanded in terms of the order parameters, includes the quadratic coupling between the order parameters in the mean field model. The δ_{loc} - ε transition¹² is considered as a first order by expanding the free energy in terms of the order parameters up to the sixth order. The phase line equations are derived from the free energies for the transitions of fluid-solid and solid-solid in this molecular crystal and they are fitted to the experimental T-P phase diagrams.^{12,14,16}

Below, in section 2 we give an outline of the theory to introduce the mean field models. Section 3 gives our calculations and results. Discussion and conclusions are given in sections 4 and 5, respectively.

THEORY

Transitions of the fluid-solid N₂ and the δ - δ_{loc} - ε can be described by the mean field models. By expanding the free energies of the solid phases of N₂ in terms of the order parameters and using the minimization conditions, the order parameter can be obtained as functions of temperature and pressure. This is done by assuming the temperature and pressure dependence of the coefficients given

in the free energies of the phases. Phase line equations for the fluid-solid transition and also for the δ - δ_{loc} - ε transitions in nitrogen can then be derived in terms of the coefficients, which predict the P-T phase diagram in this molecular system. Below the first order fluid-solid transition, second order δ - δ_{loc} and the first order δ_{loc} - ε transitions in nitrogen are considered using the mean field models.

Fluid-Solid transition

Fluid-solid transition in nitrogen can be described using a mean field model by expanding the free energy of the solid phase of N₂ in terms of the order parameter η as

$$F_S = a_2\eta^2 + a_3\eta^3 + a_4\eta^4 \quad (2.1)$$

where the coefficients ($a_2 > 0$, $a_3 < 0$ and $a_4 > 0$) are assumed to be temperature and pressure dependent. So that the free energy expanded in terms of the order parameter η with the cubic term $a_3\eta^3$ ($a_3 < 0$) as the negative energy, describes the first order transition by adding positive energy with the $a_4\eta^4$ ($a_4 > 0$) term to the molecular nitrogen for its fluid-solid transition.

By minimizing the free energy F_s with respect to the order parameter (η) according to $\partial F / \partial \eta = 0$, we get

$$2a_2 + 3a_3\eta + 4a_4\eta^2 = 0 \quad (2.2)$$

In the presence of the cubic term (Eq.2.1), we can use the condition for the first order fluid-solid transition in N₂ as

$$F_S = F_{liquid} = 0 \quad (2.3)$$

since there is no ordering in the fluid phase. This then gives

$$a_2\eta^2 + a_3\eta^3 + a_4\eta^4 = 0 \quad (2.4)$$

Solving Eqs. (2.2) and (2.4) for η , one gets

$$\eta = -2a_2/a_3 = -a_3/2a_4 \quad (2.5)$$

Thus, the phase line equation for the first order fluid-solid transition in N₂ can be obtained as

$$a_3^2 = 4a_2a_4 \quad (2.6)$$

δ - δ_{loc} - ε transitions

With decreasing temperature and/or increasing pressure at the δ - δ_{loc} transition, since the majority of disk molecules experience progressive ordering while a fraction of them maintains the same

disorder as in the δ phase [12], this transition can be considered as of a second order. So, the disordered δ phase and the partially-ordered δ_{loc} phase can be described by the disorder parameter σ and the order parameter κ respectively. As the temperature decreases and/or the pressure increases from the disordered δ phase to the partially-ordered δ_{loc} phase due to the increase in the ordering of the N_2 molecules as stated above, the disorder parameter σ (δ phase) can couple with the order parameter κ (δ_{loc} phase). In the mean field model, a quadratic coupling ($\sigma^2 \kappa^2$) is considered for the second order δ - δ_{loc} transition in nitrogen.

$$F_{\delta-\delta_{loc}} = b_2 k^2 + b_4 k^4 + c_2 \sigma^2 + c_4 \sigma^4 + d \sigma^2 k^2 \quad (2.7)$$

In this equation, the coefficients b_2 , b_4 , c_2 , c_4 and the coupling constant d are assumed to depend on temperature and pressure. For the second order δ - δ_{loc} transition in N_2 , those coefficients are taken all positive. Since δ - δ_{loc} exhibits a second order transition, the free energy (Eq.2.7) has got the positive energy with the terms of $b_4 k^4$ and $c_4 \sigma^4$. Additional positive terms up to the sixth power such as the disorder parameter $c_6 \sigma^6$ (δ phase) or the order parameter $b_6 \kappa^6$ (δ_{loc} phase) correspondingly an additional energy to the molecular nitrogen are not needed in the mean field model. Notice that the coupling term is also to the fourth power ($d \sigma^2 \kappa^2$) as the other fourth power terms in Eq.(2.7). By minimizing the free energy with respect to the order parameter κ and the disorder parameter σ ,

$$\frac{\partial F}{\partial \kappa} = 2\kappa(b_2 + 2b_4 \kappa^2 + d\sigma^2) = 0 \quad (2.8)$$

and

$$\frac{\partial F}{\partial \sigma} = 2\sigma(c_2 + 2c_4 \sigma^2 + d\kappa^2) = 0 \quad (2.9)$$

respectively. Solutions for Eq.(2.8) give $\kappa=0$ when $b_2 + d\sigma^2 \neq 0$, which leads to the disordered δ phase in nitrogen. It also gives that

$$b_2 + 2b_4 \kappa^2 + d\sigma^2 = 0 \quad (2.10)$$

when $\kappa \neq 0$, which defines the δ_{loc} phase. Since the δ_{loc} is a partially-ordered phase including disordering with the disorder parameter σ (δ phase) while the ordering is growing as stated before, Eq.(2.10) gives us

$$F_{\delta-\delta_{loc}} = b_2 \kappa^2 + b_4 \kappa^4 + c_2 \left(-\frac{b_2}{d} - \frac{2b_4}{d} \kappa^2 \right) + c_4 \left(-\frac{b_2}{d} - \frac{2b_4}{d} \kappa^2 \right)^2 + d \kappa^2 \left(-\frac{b_2}{d} - \frac{2b_4}{d} \kappa^2 \right) \quad (2.15)$$

This can be arranged as follows:

$$F_{\delta-\delta_{loc}} = \frac{b_2}{d} \left(\frac{b_2 c_4}{d} - c_2 \right) + \frac{2b_4}{d} \left(\frac{2b_2 c_4}{d} - c_2 \right) \kappa^2 + b_4 \left(\frac{4b_4 c_4}{d^2} - 1 \right) \kappa^4 \quad (2.16)$$

As the temperature decreases further down and/or pressure increases, the partially-ordered δ_{loc} phase transforms into the completely-ordered ε phase with the order parameter ρ . The δ_{loc} - ε transition is considered as of a first order in nitrogen molecule.

δ - δ_{loc} transition

Free energy including both the order parameter κ (δ_{loc} phase) and the disorder parameter σ (δ phase) for the δ - δ_{loc} transition in N_2 , can be written in the mean field model with the quadratic coupling ($\sigma^2 \kappa^2$) as

$$\sigma^2 = -\frac{b_2}{d} - \frac{2b_4}{d} \kappa^2 \quad (2.11)$$

Also, solution of Eq.(2.9) gives that $\sigma = 0$ when $c_2 + d\kappa^2 \neq 0$, which defines the δ_{loc} phase with the non-zero order parameter κ . The other solution of Eq. (2.9) can be obtained from

$$c_2 + 2c_4 \sigma^2 + d\kappa^2 = 0 \quad (2.12)$$

when $\sigma \neq 0$ for the disordered δ phase which can also include some ordering growing as δ transforms into the δ_{loc} phase. By substituting Eq.(2.11) into Eq.(2.12), one gets the order parameter κ of the δ_{loc} phase as

$$\kappa^2 = \frac{2b_2 c_4 - c_2 d}{d^2 - 4b_4 c_4} \quad (2.13)$$

By means of Eq.(2.13), the disorder parameter σ of the δ phase can be obtained as

$$\sigma^2 = -\frac{b_2}{d} - \frac{2b_4}{d} \left(\frac{2b_2 c_4 - c_2 d}{d^2 - 4b_4 c_4} \right) \quad (2.14)$$

in terms of the coefficients of the free energy (Eq.2.7). This free energy then becomes in terms of the order parameter κ (δ_{loc} phase) by substituting Eq.(2.11) into Eq.(2.7) as

In Eq. (2.16), the first term describes disordering in the free energy at various temperatures and pressures in nitrogen. From the free energy in the form of Eq. (2.16), the phase line equation can be derived by using the condition for the second order transition (δ - δ_{loc}) as

$$\frac{2b_4}{d} \left(\frac{2b_2c_4}{d} - c_2 \right) = 0 \quad (2.17)$$

Since $2b_4/d \neq 0$, we then have

$$2b_2c_4 = c_2d \quad (2.18)$$

as the phase line equation for the δ - δ_{loc} transition in nitrogen.

δ_{loc} - ε transition

The δ_{loc} - ε transition is considered as of a first order as stated above by expressing the free energies of the δ_{loc} and ε phases in terms of the order parameters κ and ρ , respectively,

$$F_\delta(loc) = b_2\kappa^2 + b_4\kappa^4 + b_6\kappa^6 \quad (2.19)$$

and

$$F_\varepsilon = e_2\rho^2 + e_4\rho^4 + e_6\rho^6 \quad (2.20)$$

where the coefficients b_2 , b_4 , b_6 , and e_2 , e_4 , e_6 , are assumed to be dependent on the temperature and pressure, as before.

For the first order δ_{loc} - ε transition, the coefficients are $b_2 > 0$, $b_4 < 0$ and $b_6 > 0$ for $F_\delta(loc)$, and $e_2 > 0$, $e_4 < 0$ and $e_6 > 0$ for F_ε . By using the minimization condition that $\frac{\partial F_\delta(loc)}{\partial \kappa} = 0$ and $\frac{\partial F_\varepsilon}{\partial \rho} = 0$, one gets

$$b_2\kappa^2 + b_4\kappa^4 + b_6\kappa^6 = 0 \quad (2.21)$$

and

$$e_2\rho^2 + e_4\rho^4 + e_6\rho^6 = 0 \quad (2.22)$$

Quadratic equations in κ^2 and ρ^2 (Eq.2.21 and 2.22) can be solved under the ansatz $b_2b_6/b_4^2 \ll 1$ and $e_2e_6/e_4^2 \ll 1$, which gives

$$\kappa^2 = -b_2 / 2b_4 \quad (2.23)$$

and

$$\rho^2 = -e_2 / 2e_4 \quad (2.24)$$

Substituting κ^2 (Eq.2.23) and ρ^2 (Eq.2.24) into the free energies of $F_\delta(loc)$ (Eq.2.19), and F_ε (Eq.2.20), respectively, gives

$$F_\delta(loc) = -\frac{b_2^2}{4b_4} - \frac{b_2^3b_6}{8b_4^3} \quad (2.25)$$

and

$$F_\varepsilon = -\frac{e_2^2}{4e_4} - \frac{e_2^3e_6}{8e_4^3} \quad (2.26)$$

By using the condition for the first order δ_{loc} - ε transition in N_2 ,

$$F_\delta(loc) = F_\varepsilon \quad (2.27)$$

Eqs. (2.25) and (2.26) then give

$$\frac{b_2^2}{b_4} \left(1 + \frac{b_2b_6}{2b_4^2} \right) = \frac{e_2^2}{e_4} \left(1 + \frac{e_2e_6}{2e_4^2} \right) \quad (2.28)$$

This is the phase line equation for the first order δ_{loc} - ε transition in nitrogen.

CALCULATION OF THE PHASE DIAGRAM

T-P phase diagrams of the fluid-solid (melting temperatures at high pressures) and of the δ - δ_{loc} - ε phase transitions were calculated for nitrogen. For this calculation, the phase line equations were used as derived from the free energies of those transitions. By employing the temperature and pressure dependence of the coefficients, the phase line equations were fitted to the experimental data for the transitions studied in nitrogen.

Fluid-Solid Transition

For the first order fluid-solid transition in nitrogen, the temperature and pressure dependence of the coefficients a_2 and a_3 were assumed as

$$a_2 = a_{20}(T - T_m) \quad (3.1)$$

$$a_3 = a_{30}(P - P_m) \quad (3.2)$$

with constant a_4

$$a_4 = a_{40} \quad (3.3)$$

where a_{20} , a_{30} and a_{40} are all constants. T_m and P_m denote the melting temperature and pressure, respectively. Using the temperature and pressure dependence of the coefficients (Eqs. 3.1–3.3), the order parameter η of the solid phase (Eq. 2.5) was obtained as

$$\eta = -\frac{2a_{20}}{a_{30}} \left(\frac{T - T_m}{P - P_m} \right) = \frac{-a_{30}}{2a_{40}} (P - P_m) \quad (3.4)$$

By means of the phase line equation (Eq.2.6), one gets

$$a_{30}^2 (P - P_m)^2 = 4a_{20}a_{40} (T - T_m) \quad (3.5)$$

By expanding Eq. (3.5), the functional form was expressed as

$$f(T, P) = T - \alpha_1 - \alpha_2 P + \alpha_3 P^2 = 0 \quad (3.6)$$

where

$$\alpha_1 = T_m + \frac{a_{30}^2 P_m}{2a_{20}a_{40}} \quad (3.7)$$

$$\alpha_2 = -\frac{a_{30}^2 P_m}{2a_{20}a_{40}} \quad (3.8)$$

$$\alpha_3 = -\frac{a_{30}^2}{4a_{20}a_{40}} \quad (3.9)$$

which can be expressed as

$$\alpha_1 = T_m - \alpha_3 P_m^2 \quad (3.10)$$

and

$$\alpha_2 = 2\alpha_3 P_m \quad (3.11)$$

Eq.(3.6) was then fitted to the observed T-P data with the maximum values of $T_m=1769.4$ K

and $P_m=74.3$ GPa on the melting line¹⁶ for the fluid-solid transition in nitrogen.

The fitted parameters α_1 , α_2 and α_3 within the pressure intervals are given in Table 1. We plot the T-P phase diagram (Eq.3.6) and the observed data¹⁶ with uncertainties in Fig. 1 for the fluid-solid transition in N₂.

A linear variation of temperature with the pressure was also fitted to the experimentally obtained T-P data¹⁴ according to the phase line equation (Eq.2.6) for the melting temperatures at high pressures in N₂ by using the maximum values of $T_m=1920$ K and $P_m=50$ GPa. By assuming the temperature and pressure dependence of the parameters for the melting temperatures and pressures as

$$a_2 = a_{20}(T - T_m) \quad (3.12)$$

$$a_3 = a_{30}(T - T_m) \quad (3.13)$$

$$a_4 = a_{40}(P - P_m) \quad (3.14)$$

Table 1

Values of the fitted parameters within the pressure intervals indicated for the fluid-solid transition¹⁶ and the melting curves¹⁴ according to Eq. (3.6), and for the solid-solid transitions of δ - δ_{loc} and δ_{loc} - ϵ ¹² according to Eq. (3.25) in N₂

$f(T, P)$	$\alpha_1(K)$	$\alpha_2 \times 10^{-2}$ (K/GPa)	$\alpha_3 \times 10^{-3}$ (K/GPa ²)	Pressure interval (GPa)
Fluid-Solid transition	43.16	-7.1	4.80	15.9 < P < 74.3
Melting curves	200.98	3599.0	-	0.2 < P < 49.7
	3180.45	-2501.0	-	49.5 < P < 71.2
δ - δ_{loc}	-4.44	4.12	3.11	3.9 < P < 21.4
δ_{loc} - ϵ	-1.98	3.78	3.84	5.5 < P < 33.6

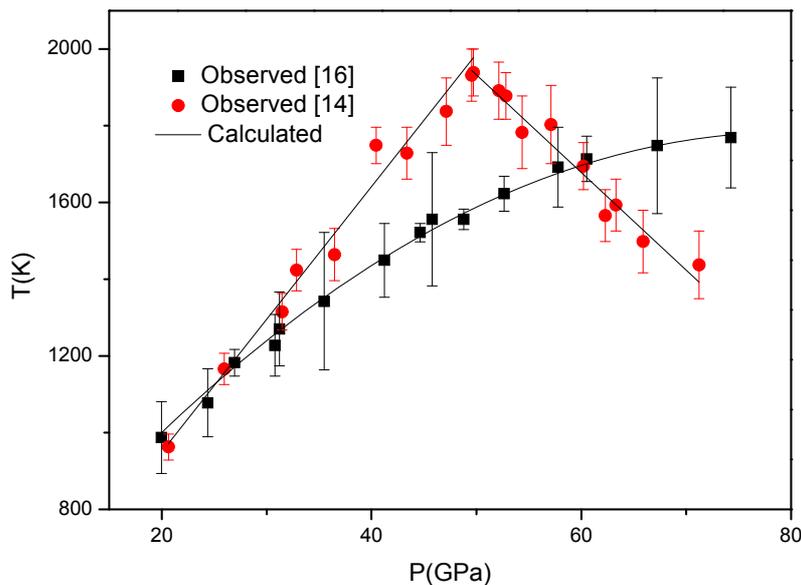


Fig. 1 – Calculated phase diagram of N₂ in the melting region according to Eq.(3.6) by using the mean field model. Observed data (squares)¹⁶ and (circles)¹⁴ with the uncertainties are also given for the fluid-solid transition in nitrogen.

the order parameter η (Eq.2.5) can be written as

$$\eta = -\frac{a_{30}}{2a_{40}} \left(\frac{T - T_m}{P - P_m} \right) = -\frac{2a_{20}}{a_{30}} \quad (3.15)$$

for the melting temperatures at high pressures. This indicates that the temperature and pressure dependence of the order parameter η in the ordered phase (solid N₂) coincides with a constant value of η in the disordered phase (liquid N₂) in this molecular crystal.

On the basis of the temperature and pressure dependence of the coefficients (Eqs.3.12–3.14), the T-P phase diagram was obtained for the melting temperatures at high pressures according to the phase line equation (Eq. 2.6) in nitrogen. By substituting Eqs. (3.12–3.14) into Eq. (2.6), we get

$$a_{30}^2 (T - T_m) = 4a_{20}a_{40} (P - P_m) \quad (3.16)$$

By expanding Eq. (3.16), one gets Eq. (3.6) with the $\alpha_3 = 0$, where

$$\alpha_1 = T_m - \left(\frac{4a_{20}a_{40}}{a_{30}^2} \right) P_m \quad (3.17)$$

and

$$\alpha_2 = \left(\frac{4a_{20}a_{40}}{a_{30}^2} \right) \quad (3.18)$$

or

$$\alpha_1 = T_m - \alpha_2 P_m \quad (3.19)$$

Eq. (3.6) with the coefficients α_1 (Eq.3.17), α_2 (Eq.3.19) and $\alpha_3 = 0$, was fitted to the experimental T-P data¹⁴ in the two pressure intervals with the parameters as given in Table 1. This is plotted in Fig.1 for the melting temperature of nitrogen.

δ - δ_{loc} - ε transitions

For the δ - δ_{loc} (second order) and δ_{loc} - ε (first order) transitions, temperature and pressure dependence of the order parameters κ (δ_{loc} phase), and ρ (ε phase), and the disorder parameter σ (δ phase) were obtained. Also, the phase line equations were fitted to the observed T-P data [12] and the fitted parameters for those solid-solid transitions were determined.

δ - δ_{loc} transition

By assuming the temperature (T) and pressure (P) dependence of the coefficients as

$$b_2 = b_{20} (T - T_c) \quad (3.20)$$

$$b_4 = b_{40} (T - T_c) \quad (3.21)$$

$$c_2 = c_{20} (P - P_c) \quad (3.22)$$

$$c_4 = c_{40} (P - P_c) \quad (3.23)$$

and taking the quadratic coupling d (Eq. 2.7) as constant for the δ - δ_{loc} transition in N₂, the order parameters (squared) κ^2 of the δ_{loc} phase (Eq. 2.13) and the σ^2 of the δ phase (Eq. 2.14) were obtained as functions of T and P. The T-P phase diagram of this transition was predicted from the phase line equation Eq. 2.18), which gives

$$2b_{20}c_{40} (T - T_c)^2 = c_{20}d (P - P_c) \quad (3.24)$$

By expanding Eq. (3.24), the functional form was obtained as

$$f(T, P) = P - \alpha_1 - \alpha_2 T + \alpha_3 T^2 = 0 \quad (3.25)$$

where

$$\alpha_1 = P_c + \left(\frac{2b_{20}c_{40}}{c_{20}d} \right) T_c^2 \quad (3.26)$$

$$\alpha_2 = -\left(\frac{2b_{20}c_{40}}{c_{20}d} \right) T_c \quad (3.27)$$

$$\alpha_3 = \frac{2b_{20}c_{40}}{c_{20}d} \quad (3.28)$$

which was expressed in the form of

$$\alpha_1 = P_c + \alpha_3 T_c^2 \quad (3.29)$$

and

$$\alpha_2 = -2\alpha_3 T_c \quad (3.30)$$

Eq.(3.25) was fitted to the experimental data¹² and the fitted parameters were determined as given in Table 2. We plot in Fig. 2 the T-P phase diagram according to Eq. (3.25) with the experimental data for the δ - δ_{loc} transition in nitrogen.

δ_{loc} - ε transition

Considering the phase line equation (Eq.2.28) for this transition, the temperature and pressure dependence of the coefficients were assumed as

$$b_2 = b_{20} (T - T_c) \quad (3.31)$$

$$b_4 = b_{40} (P - P_c) \quad (3.32)$$

$$b_6 = b_{60} (T - T_c)(P - P_c) \quad (3.33)$$

for the δ_{loc} phase and

$$e_2 = e_{20} (T - T_c) \quad (3.34)$$

$$e_4 = e_{40} (P - P_c) \quad (3.35)$$

$$e_6 = e_{60} (T - T_c)(P - P_c) \quad (3.36)$$

Table 2

Values of the slope(dP/dT) within the temperature and pressure intervals according to the equations indicated for the transitions in N_2 . T_c and P_c denote maximum (T_m, P_m) values for the melting curve and fluid –solid transition (Fig. 1). dT/dP values are calculated at 300 K for the δ - δ_{loc} and δ_{loc} - ϵ transitions in N_2

Transition in N_2	T_c (K)	P_c (GPa)	dT/dP (K/GPa)	Temperature Interval (K)	Pressure Interval (GPa)	Ref. No.	Eq. No.
Melting Curves	1920.0	50.0	34.6 ($T < T_c$)	74.57 < $T < 1939.0$	0.2 < $P < 49.7$	14	3.6
			-25.5 ($T > T_c$)	1437.3 < $T < 1932.2$	49.5 < $P < 71.2$		
Fluid-Solid	1746.7	74.0	-0.0638	816.0 < $T < 1769.41$	15.9 < $P < 74.3$	16	3.6
δ - δ_{loc}	300.0	10.72	16.7	181.2 < $T < 463.3$	3.9 < $P < 21.4$	12	3.25
δ_{loc} - ϵ	300.0	17.35	16.4	100.4 < $T < 534.8$	5.5 < $P < 33.6$	12	3.25

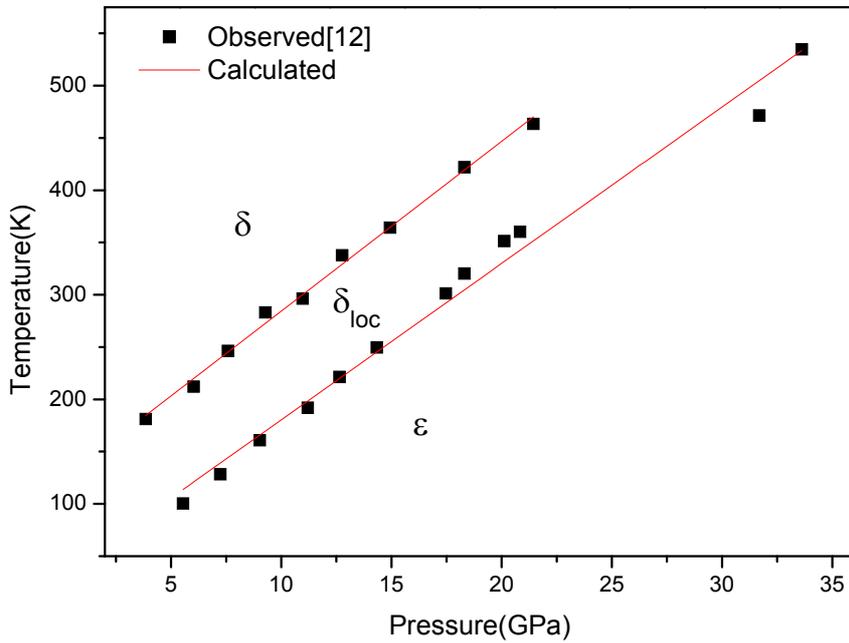


Fig. 2 – Calculated phase diagram of N_2 for the transitions of δ - δ_{loc} and δ_{loc} - ϵ according to Eq.(3.25) using the experimental data.¹²

for the ϵ phase in N_2 . Using those functional forms of the coefficients, the temperature and pressure dependence of the order parameters (squared) κ^2 (Eq.2.23) and ρ^2 (Eq.2.24) of the phases δ_{loc} and ϵ , respectively, were obtained for the δ_{loc} - ϵ transition in nitrogen. By substituting the functional forms of the coefficients (Eq. 3.31–3.36) into the phase line equation (Eq.2.28), the T-P phase diagram of the δ_{loc} - ϵ transition was predicted. This gives the same as the δ - δ_{loc} transition (Eq.3.25) with the definition of the parameters as

$$\alpha_1 = P_c - T_c^2 \left(\frac{b_{20}^3 b_{60}}{2b_{40}^3} - \frac{e_{20}^3 e_{60}}{2e_{40}^3} \right) / \left(\frac{b_{20}^2}{b_{40}} - \frac{e_{20}^2}{e_{40}} \right) \quad (3.37)$$

$$\alpha_2 = 2T_c \left(\frac{b_{20}^3 b_{60}}{2b_{40}^3} - \frac{e_{20}^3 e_{60}}{2e_{40}^3} \right) / \left(\frac{b_{20}^2}{b_{40}} - \frac{e_{20}^2}{e_{40}} \right) \quad (3.38)$$

$$\alpha_3 = - \left(\frac{b_{20}^3 b_{60}}{2b_{40}^3} - \frac{e_{20}^3 e_{60}}{2e_{40}^3} \right) / \left(\frac{b_{20}^2}{b_{40}} - \frac{e_{20}^2}{e_{40}} \right) \quad (3.39)$$

which then gives the same relations as Eqs.(3.29) and (3.30) for the δ - δ_{loc} transition. By fitting Eq.(3.25) to the experimental data¹² with the parameters (Eqs.3.37-3.39) determined (Table 2), the T-P phase diagram was obtained for the δ_{loc} - ϵ transition in nitrogen, as given in Fig. 3.

DISCUSSION

In the first part of this study, the T-P phase diagram of the solid-fluid transition in nitrogen was calculated by the mean field model with the cubic term of the order parameter (η^3) in Eq. (2.1), which describes a first order transition. Using Eq.

(3.6), quadratic fit to the experimental data¹⁶ and linear fits to the experimental data¹⁴ with the uncertainties below and above the maximum temperature, were employed to describe the solid-fluid transition and to calculate the melting temperatures (Fig. 1) in nitrogen. For the first order fluid-solid transition in nitrogen, it has been measured¹⁶ that the temperature increases continuously with increasing pressure up to about 90 GPa in the region of melting in nitrogen (Fig. 1). The melting temperature rises linearly up to a maximum at 50 GPa and 1920 K, and with increasing pressure it suddenly decreases linearly to 1400 K and 71 GPa (Fig.1) as observed experimentally.¹⁴ From the linear fits the dT/dP values which were obtained (Table 2), agree with the previous values of 35 K/GPa and -27 K/GPa¹⁴ below and above the maximum melting temperatures, respectively, in nitrogen. The negative slope (dT/dP) above 50 GPa (Fig. 1) implies that the liquid is denser than the underlying solid, as indicated previously.¹⁴ The sharpness of the changes suggests that the transition is first order and is a liquid-liquid polymer transition.¹⁴ This has also been suggested from the molecular dynamics simulations by providing evidence for the existence of a phase transition from molecular to polymeric liquid nitrogen.²⁶

There occur the differences between the experimental data of Refs. 16 and 14 due to the different methods used to determine the melting curve, namely, Raman spectroscopy employed and visual observations from laser speckle motion exclusively to determine the melting transition, respectively, as also pointed out previously.¹⁶ The temperature was determined from optical pyrometry in both studies. Consequently, the melting data of Ref.16 are different in both temperature and pressure for most of the melt range except below about 30 GPa in comparison to the melting line of Ref.14 which reported as the linear extension of Ref.15 with a sharp melting maximum at 50 GPa and 1920 K and subsequent linear decrease in the melt line¹⁶ as shown in Fig. 1. Above 30 GPa, the melt line diverges as compared to the melt data of Ref.16 exhibiting a slight curvature and slow turnover in the melt curve giving a broad melting maximum¹⁶ as also stated above (Fig. 1).

Since the temperature increases continuously (smoothly) with increasing pressure up to the maximum (T_m and P_m), then it tends to decrease slightly almost independent of temperature for the

fluid-solid transition (Fig.1), the temperature and the pressure dependence of the coefficients a_2 and a_3 were chosen as Eqs.(3.1) and (3.2), respectively, and a_4 as a constant (Eq.3.3) to fit to the experimental data¹⁶ adequately in the mean field model. However, the T-P experimental data¹⁴ obtained almost in the same temperature and pressure interval show completely different behavior *i.e.* temperature increases up to ~50 GPa and then decreases sharply linearly with the pressure, as stated above. Due to this unusual behavior of T versus P of Ref.14 the temperature dependence of the coefficients a_2 and a_3 were chosen (Eqs. 3.12 and 3.13) the same as Eq. (3.1), whereas the coefficient a_4 was assumed to depend on the pressure (Eq.3.14) which is the same as Eq.(3.2) in order to describe the experimental data¹⁴ satisfactorily in the mean field model. The choice of the coefficients a_2 , a_3 and a_4 was the best among the other possibilities to fit to the experimental data.¹⁴

In the second part of our study, the T-P phase diagram was calculated for the δ - δ_{loc} transition (Fig.2) by using the mean field model with the quadratic coupling ($\sigma^2 \kappa^2$) in Eq. (2.7) as it was considered as of a second order transition. The T-P phase diagram was also calculated as suggested from the first detection by the Raman spectroscopy^{27,28} for the δ_{loc} - ϵ transition (Fig.2) by using the mean field model with the free energies (Eqs.2.19 and 2.20), which was considered as of a first order transition in nitrogen, as also described previously. For both calculations, Eq.(3.25) was fitted to the experimental data with the parameters determined (Table 1), which agree with the previous analysis by using the quadratic dependence of the pressure on the temperature, $P(T)$, as Eq.(3.25).¹² As stated above, δ phase undergoes the δ_{loc} phase as a second order transition²⁷ which is connected with changes to the orientational behavior of the N_2 molecules from a free rotation into an orientationally localized mode (10.5 GPa, 300 K). With decreasing temperature and/or increasing pressure, the molecules partially order in a δ - N_2 phase and then completely in ϵ - N_2 .²⁹ Both δ and δ_{loc} phases are dynamically ordered and the δ_{loc} phase is characterized by a progressive ordering of the disk molecules with decreasing temperature,¹² as also mentioned before. On the other hand, the temperature of the δ_{loc} - ϵ transition is more uncertain due to a significant hysteresis as observed experimentally, which demonstrates the metastability of one phase into

the other.¹² It has been reported that the ε phase becomes stable at 16 GPa at room temperature.^{11,18,19} Theoretical calculations confirm the stability of the ε phase as the ordered phase in the 2-40 GPa range.³⁰

When the T-P phase diagrams were calculated between the solid and fluid phases and melting temperatures (Fig. 1) and, for the transitions of δ - δ_{loc} and δ_{loc} - ε in nitrogen (Fig.2), the temperature and pressure dependence of the coefficients given in the free energies, were used in the phase line equations as stated above. Not only the phase line equations which predict the T-P phase diagram in N_2 , but also the temperature and pressure dependence of the order parameter as derived here, and of the other thermodynamic functions such as susceptibility, entropy, heat capacity, thermal expansion and isothermal compressibility can be obtained for the transitions studied in nitrogen. Functional forms of those thermodynamic quantities can be derived from the free energies of the mean field models presented here under the assumptions of the coefficients in nitrogen. Calculated thermodynamic quantities can then be compared with the observed data for those transitions studied in this molecular crystal. Due to some striking similarities between the phase diagrams of nitrogen and its other neighboring element carbon,³¹ which both have completely different bonding properties at low pressure, they have a melting maximum and transform to the diamond structure at high pressure.¹⁴ Melting curves of carbon can also be predicted by using the mean field models presented here.

CONCLUSIONS

The T-P phase diagrams were calculated for the solid-fluid transition, melting temperatures at high pressures and for the transitions of the δ - δ_{loc} and δ_{loc} - ε in nitrogen by using the mean field models. The phase line equations derived from the free energies, were fitted to the experimental data from the literature by assuming the temperature and pressure dependence of the coefficients given in the free energies.

Our results show that the mean field model with the cubic term of the order parameter (first order transition) for the solid-fluid transition and for the melting temperatures at high pressures in nitrogen is satisfactory. We also find that the mean field models with the quadratic coupling between the

order parameters (second order transition) and with the sixth-power of the order parameters (first order transition) in the free energy expansion describe adequately the solid-solid transitions of δ - δ_{loc} and δ_{loc} - ε , respectively, in molecular nitrogen.

This method of calculating the T-P phase diagrams by using the mean field theory can also be applied to some other molecular crystals.

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