

Phase transition line of solid molecular nitrogen into CG-polymeric phase

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The coexistence line of two high-pressure phases of solid nitrogen: molecular and polymeric cubic gauche (CG) has been predicted using two separate equations of state. Phase transition parameters: latent heat, volume and entropy jumps were calculated. At low temperature the predicted volume jump $\Delta V(P)$ is in agreement with recent experimental data; at elevated temperatures $P(T)$ -curve tends to the vicinity of the pressure maximum on the melting line.

PACS: 05.70.Fh Phase transitions: general studies;
61.50.Ks Crystallographic aspects of phase transformations; pressure effects;
64.10.+h General theory of equations of state and phase equilibria.

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1. Introduction

First experimental evidence of an unusual behavior of highly compressed molecular nitrogen was obtained by Nellis and co-workers [1] who studied liquid nitrogen compressed by a strong shock wave to density characteristic of the crystal at low temperatures. The “shock cooling” effect observed in this work was interpreted as a result of a phase transformation of dense molecular N_2 into a monatomic phase. This phase was predicted by McMahan and Le Sar [2] in 1985 and re-considered as a polymeric structure by Martin and Needs [3] and Mailhot *et al.* [4]. These works have triggered experimental studies and *ab initio* calculations which continue up to now [5,6]. The stability and structure of high-pressure phases of nonmolecular solid nitrogen at low and elevated temperatures were studied by Gregoryanz *et al.* [7], Goncharov *et al.* [8], Eremets *et al.* [9]. These optical studies demonstrated that the molecular-to-atomic transition can be interpreted as the result of breaking of the triple chemical bond in N_2 with the subsequent formation of three ordinary chemical bonds with three nearest neighbors. It was found that the most likely structure of the nonmolecular nitrogen solid both in crystalline and amorphous states has the polymeric cubic gauche (CG) [4] coordination. Serious difficulties arising in experiment [8] at elevated temperature prevent precise localization of the position of the transition line between molecular and crystalline polymeric phases on the phase diagram of solid nitrogen and its stability is still under debate.

In our previous paper [10] we performed Monte Carlo simulations of atomic nitrogen, and proposed in Ref. 11 the equation of state (EOS) for the CG polymeric phase based on these simulations. In principle, when combined with EOS for molecular phase, these two equations allow to estimate the temperature of molecular-to-polymeric transition as a function of pressure. Such an attempt was already made in our old paper [12], where we considered a different structure of the polymeric phase *A7* [3], which was found later to be less stable than the CG structure [4]. A great amount of new experimental data and theoretical calculations obtained since then provide a reason for reconsidering this problem using EOS for polymeric phase [11].

The aim of this paper is to estimate the pressure–temperature relationship and the volume jump at the transition from molecular to polymeric CG solid phases at low temperatures. In these calculations the EOS of the classical crystal from our paper [12] and estimates of energy differences between polymeric and molecular solids at $T = 0$ from Refs. 4, 5 have been used. In Secs. 2 and 3 we describe briefly the EOS for both molecular and polymeric phases. In Sec. 3 details of the phase equilibrium calculations are presented and the results are compared with existing experimental data. In Sec. 4 we discuss these results and the effect of the structure of the polymer phase on the position of the molecular-to-polymer transition line.

2. Equation of state of molecular phase

According to Refs. 7, 8, the structure of the high-pressure ζ -N₂ molecular phase, preceding the polymerization transition on the phase diagram of solid nitrogen, is known insufficiently. Following to Ref. 12, we assumed that the structure of the molecular phase is similar to that of β -O₂. Such a structure can be produced from *A7* lattice by shifting its sublattices along the direction [111] until the atoms approach one another to form pairs and then by rotating the axes of these pairs in the direction [100]. We applied the same atom–atom force model for molecular crystal as was proposed in Ref. 12. The nonvalence repulsion of all atoms was described by the inverse-power law

$$\Phi(R) = AR^{-13/2}, \quad (1)$$

where $A/k = 3.86 \cdot 10^5$ K and the interatomic distance R is in angstroms.

The “valence” attraction of the atoms bounded by the triple bond in N₂ molecules, $\Delta U_3(R)$, is defined in harmonic approximation as

$$\Phi(R) + \Delta U_3(R) = -D_e + C(R - R_e)^2. \quad (2)$$

Here D_e is the dissociation energy of N₂ into two isolated N atoms, C is the elastic constant, and R_e is the equilibrium length of the triple N \equiv N bond. All parameters in Eq. (2) were adopted from known spectroscopic and thermochemical gas phase data [12] (see Table 1).

Table 1. Interaction parameters adopted in calculations

Parameter	Value	Units
A/k	$3.86 \cdot 10^5$	K
C/k	$8.38 \cdot 10^5$	K
R_e	1.1	Å
D_e/k	$1.15 \cdot 10^5$	K
γ_0	30.5	–
ρ_0^{-1}	7.0	cm ³ /mol
$\theta_D^{(0)}$	200	K

The total interaction energy of molecular crystal consists of the intermolecular and intramolecular contributions:

$$U_{\text{mol}} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \Phi(R_{ij}) + \frac{1}{2} \sum_{k=1}^N \Delta U_3(R_k). \quad (3)$$

Here the first summation runs over all pairs of atoms and the second one over atomic pairs of bonded N₂ molecules, i.e., accounts for intramolecular interactions.

Since parameters of the $\Phi(R)$ in Eq. (1) and $\Delta U_3(R)$ in Eq. (2) potentials are known, we are able to calculate thermodynamic properties of the molecular phase at nonze-

ro temperatures. We applied the same first approximation of the perturbation theory [13] as was used in Ref. 12. It yields the following expression for the excess free energy of the molecular solid:

$$F_{\text{mol}}(T, V) = -D_e + C(R_0 - R_e)^2 + U_{\text{mol}}^{\text{rep}}(R_0) - kT \ln(v_f^{\text{mol}}/V), \quad (4)$$

where v_f^{mol} and V are the free and specific volume per atom, respectively; R_0 is the equilibrium interatomic distance in N₂ molecules at the given volume V and temperature T , and the repulsive contribution to the static lattice energy $U_{\text{mol}}^{\text{rep}}(R_0)$ is defined as follows [12]:

$$U_{\text{mol}}^{\text{rep}}(R_0) = \Phi(a) \left[S_{6.5}^{\text{sc}} + \left(\alpha_0^{\text{sc}} - \alpha_0^{\text{fcc}} - \frac{195}{8} \right) \left(\frac{R_0}{a} \right)^2 - 1 + \frac{13}{2} \frac{R_0}{a} \right] + \Phi(R_0). \quad (5)$$

Here a is the equilibrium lattice parameter, $S_n = \sum_{j \geq 2} (a/R_{1j})^n$ are the lattice sums: S_n^{sc} for simple cubic structure, and S_n^{sc} for face-centered cubic sublattice

$$\alpha_0^{\text{sc}} = \frac{145}{24} A S_{6.5}^{\text{sc}} a^{-13/2},$$

$$\alpha_0^{\text{fcc}} = \frac{145}{24} A S_{8.5}^{\text{fcc}} a^2 (2\sqrt{2}V)^{-15/6}$$

are elastic constants calculated using repulsion potential Eq. (1). The free volume was calculated in harmonic approximation as

$$v_f^{\text{mol}} = \left(\frac{\pi kT}{\alpha_3} \right)^{1/4} \left(\frac{\pi kT}{\alpha_4} \right)^{5/4}, \quad (6)$$

where elastic constants α_3 and α_4 are

$$\alpha_3 = 2(\alpha_0^{\text{sc}} + C), \quad \alpha_4 = 2\alpha_0^{\text{sc}}. \quad (7)$$

The free energy of molecular solid Eq. (4) is expressed via the lattice parameter a , free volume Eq. (6), elastic constants Eq. (7) and the lattice sums, and can be easily evaluated knowing the interaction potentials parameters A , C , R_e and D_e placed in Table 1.

3. Equation of state of polymeric phase

To describe the polymeric CG phase of solid nitrogen, we applied here the modified Mie–Grüneisen model and the EOS of the anharmonic polymeric solid proposed in our previous work [11]. The Helmholtz free energy of the anharmonic solid was written as a sum

$$F_{\text{poly}} = F_{\text{poly}}^{(h)} + F_{\text{poly}}^{(\text{anh})}, \quad (8)$$

where $F^{(h)}$ is the quasi-harmonic contribution, represented by the modified Mie–Grüneisen model, and the anharmonic contribution is

$$\frac{F_{\text{poly}}^{(\text{anh})}}{RT} = -\frac{A_1(\rho)}{2}T - \frac{A_2(\rho)}{6}T^2. \quad (9)$$

Two anharmonic corrections $A_1(\rho)$ and $A_2(\rho)$ were deduced in Ref. 11 using deviations of the isochoric heat capacity known from the Monte Carlo [10] data for the CG phase from the Dulong–Petit law:

$$A_1(\rho) = -0.004918\rho^*(\rho^* - 1.0468)(\rho^* - 0.8481),$$

$$A_2(\rho) = 4.03 \cdot 10^4 \rho^*(\rho^* - 0.9666)(\rho^* - 0.8763),$$

$$\rho^* = \rho V_0, \quad V_0 = 7 \text{ cm}^3/\text{mol}.$$

As it was shown in Ref. 11, the anharmonic contributions to the heat capacity as well as to the thermal expansion and isothermal compressibility are important.

After extracting the anharmonic corrections, the quasi-harmonic thermal Grüneisen parameter $\gamma^{(h)}$ was deduced from Monte Carlo (MC) data. Surprisingly, it was found to be almost independent of temperature and decreasing almost linearly with increasing density. This linear decrease of the thermal quasi-harmonic Grüneisen parameter with density was described in Ref. 11 by a simple modification of the Mie–Grüneisen model. The general expression for the quasi-harmonic contribution to the Helmholtz free energy as a function of temperature T and volume V remains the same as in the original Mie–Grüneisen model [14]:

$$F_{\text{poly}}^{(h)}(T, V) = U_{\text{poly}}^{(0)}(V) + 3RTD_F(x_D). \quad (10)$$

Here $U_{\text{poly}}^{(0)}$ is the energy of static lattice, $D_F(x_D)$ is the Debye function

$$D_F(x_D) = \frac{3}{x_D^3} \int_0^{x_D} \ln(1 - e^{-x}) x^2 dx; \quad x_D = \frac{\theta_D}{T}. \quad (11)$$

The density-dependent Grüneisen parameter γ was defined in Ref. 11 as

$$\gamma = \frac{\partial \ln \theta_D}{\partial \ln \rho} = \gamma_0 \left(1 - \frac{\rho}{\rho_0}\right), \quad (12)$$

where ρ_0 is the density corresponding (within quasi-harmonic approximation) to $\gamma = 0$. The modified Mie–Grüneisen model contains three constants determined from MC data in Ref. 11: γ_0 , ρ_0 , and $\theta_D^{(0)} = \theta_D(\rho_0)$. All parameters were adopted from Refs. 11 and 12 and presented in Table 1.

Applying the standard thermodynamic relations one can obtain expressions for quasi-harmonic contributions to all thermodynamic functions. Equations for the energy and

heat capacity remain the same as in the original Mie–Grüneisen model, except for the new density dependence of the Debye temperature.

We adopted the explicit expression for the static lattice energy $U_{\text{poly}}^{(0)}$ proposed in Ref. 11 but shifted by ΔE_0 —the difference in energies between static molecular and static CG lattices. The value of ΔE_0 parameter is important in calculation of the phase equilibrium. Zhang *et al.* [5] refer to ΔE_0 value of 1 eV/atom. In our calculations we adopted the value $\Delta E_0 = 0.97$ eV/atom obtained by Mailhiot *et al.* [4].

4. Phase equilibrium

The phase equilibrium between atomic and molecular phases was studied numerically by the standard double-tangent method as described in Ref. 11. The orthobaric volumes V_m and V_p of coexisting molecular polymeric solids were obtained as abscissa of the tangency points of the common tangent to the curves $F_{\text{mol}}(T, V)$ (see Eq. (4)) and $F_{\text{poly}}(T, V)$ of Eq. (10) plotted against volume V at a given temperature T , and the equilibrium pressure P of the phase transition was determined as the slope of this tangent line. Results are shown and compared with existing experimental data in Figs. 1 and 2.

As one can see in Fig. 1, the calculated value of the equilibrium transition pressure decreases significantly as temperature increases. It drops from about 200 GPa at low temperatures down to 50 GPa at $T = 1500$ K where the molecular-to-polymeric transition and melting lines meet. This is in contrast with our earlier estimations for $A7$ structure [12] predicting an increase of the transition pressure. An essential difference exists also in behavior of the volumes of coexisting phases and the volume jumps. In the

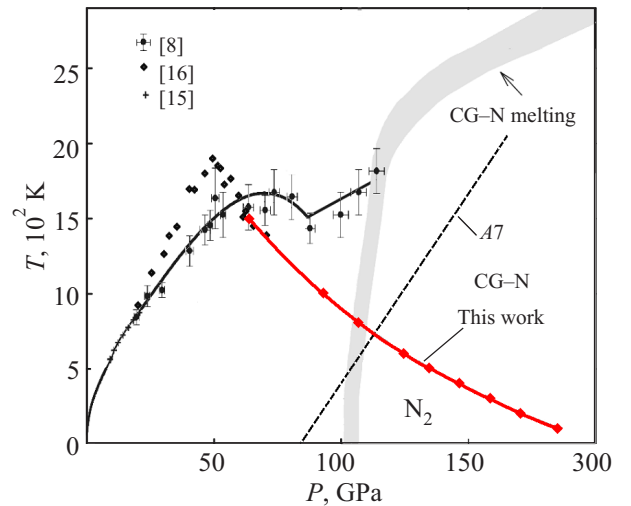


Fig. 1. Molecular-to-polymeric transition temperature–pressure dependence predicted in this work for CG-structure (red online) and the predictions for $A7$ structure (dashed line) [3]. Light grey area — melting boundary of CG–N predicted in Ref. 8. Experimental melting temperature data [8,15,16] are also shown.

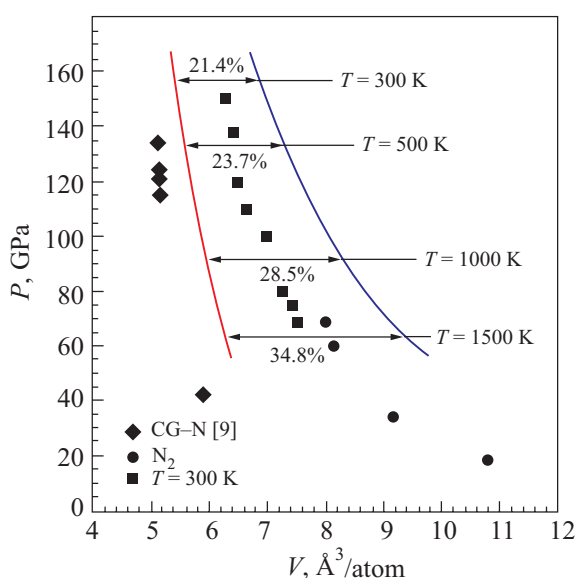


Fig. 2. Comparison of the predicted pressure–volume dependence and volume jump on the molecular-to-polymeric transition line with experimental data of Eremets *et al.* [9] at room temperature. Left (red online) and right (blue online) solid lines represent, correspondingly, predicted P – V relationship of CG-polymeric and molecular phases along transition line.

case of the $A7$ structure volumes of coexisting phases decrease slightly with decreasing temperature, while our estimates for the CG structure predict raise in both volume and the volume change with temperature (see Fig. 2).

5. Conclusions

We estimated the location of the molecular-to-polymeric transition line in solid nitrogen using two equations of state proposed earlier. The comparison of the results of this work with our previous calculations, performed for layered $A7$ structure of the polymeric phase [12] (Fig. 1) shows drastic differences in the temperature dependence of parameters of the phase transition line. In the case of the CG structure of the polymeric phase, as the temperature increases, the equilibrium transition pressure decreases and the latent heat became negative. The transition line meets the melting line at a temperature around 1500 K and the triple point appears roughly in the vicinity of the maximum of the melting temperature experimentally observed recently [8] at the pressure of about 50 GPa.

The pressure–volume dependence along the transition line, presented in Fig. 2, shows, that the molecular and polymeric orthobaric volumes, though rather overestimated, are in reasonable qualitative agreement with room-temperature measurements of Eremets *et al.* [9], in particular, the volume jump of 21.4% at $T = 300$ K is in an excellent agreement with experimental value of 22% [9].

The absolute value of the polymerization transition latent heat $|L|$ increases approximately linearly with temperature, like is the case for the $A7$ structure. That means the entropy jump L/T is nearly constant. At the same time in contrast to Ref. 12 it is negative.

At $T \sim 1000$ K the latent heat L reaches -1 eV/atom when the prediction for $A7$ structure L gives about $+0.7$ eV/atom [12]. Thus, the atomic structure of the polymeric crystalline is very important in estimation of location and parameters of the molecular-to-polymeric transition in highly compressed solid nitrogen.

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