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Calculation of the Thermodynamic Quantities for Cubic Gauche Nitrogen (cg-N)

H. Yurtseven [1*] and Ö. Akay [1, 2]

[1]Department of Physics, Middle East Technical University, 06531, Ankara-Turkey
[2]Department of Mechatronics Engineering, Faculty of Technology, Marmara University, Istanbul, -Turkey
E-mail: *hamit@metu.edu.tr

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Abstract

This work aims to investigate the thermodynamic properties of the cubic gauge nitrogen (cg-N) by calculating the relevant thermodynamic quantities as a functions of temperature and pressure. The thermodynamic quantities of volume (V), thermal expansion (α_p), isothermal compressibility (κ_T), bulk modulus(B), and the heat capacity (C_p) are calculated as a function of temperature at constants pressures (0, 35, 125, 250 GPa) for the cg-N structure. Also, the pressure dependences of V, κ_T, α_p, C_p and γ (macroscopic Grüneisen parameter) are predicted at T= 295 K for this structure. This calculation is caried out by the thermodynamic relations using some literature data. From our calculations, we find that the κ_T, α_p and also B exhibit anomalous behavior as the temperature lowers below about 100 K at constant pressures studied. This is an indication that cg-N transforms to a solid phase at low temperatures (below about 100 K). Experimental measurements can examine this prediction when available in the literature for the cg-N phase. Also, our predictions of the κ_T, α_p, C_p and γ at various pressures (T= 295 K) can be examined experimentally for the cg-N phase. This calculation method can be applied to some other structures.

Keywords: *Thermodynamic quantities; cubic gauche nitrogen; macroscopic Grüneisen parameter.*

1. Introduction

A number of molecular solids are known to undergo a transition to a nonmolecular phase under high compression [1]. Among those structures, nitrogen consists of molecules with the two atoms which are strongly triple-bonded [2]. Higher pressure transitions with the diatomic molecular state have been studied [3-5] as pointed out previously [6]. In particular, pressure-volume relations, thermal expansion coefficients, phase transition pressures and temperatures have been determined by the Monte Carlo method [3]. It has been indicated that in the pressure region of 10-100 GPa by the Raman, infrared and x-ray measurements the structural properties depend on the kinetics of the experiment and on the P_T path [5]. Pressure-induced dissociation forming a polymeric phase called cubic-gauche (cg-N) was found [2], which is a three-dimensional network structure with the $I_{2,3}$ symmetry as predicted by the theoretical calculations[7,8] as reported in an earlier study [6]. Monte Carlo calculations have been caried out for the atomic, molecular, and compressed forms of the nitrogen [8] and for the calculations of the molecular and nonmolecular structures of nitrogen, the local- density- functional method has been used [9] and the cg-N has been observed experimentally [1,7,9-11]. At high pressures and temperatures, T-P phase diagram including the phases θ and i solid nitrogen has been obtained experimentally [10]. Also, experimental measurements have been conducted to determine the P-T path [11]. It has been indicated that the cg-N represents a new class of single-bonded nitrogen material with unique properties such as energy capacity [2]. It has also been indicated that polymeric nitrogen with a cg- structure grows in single crystals if the pressure-temperature conditions are close to the boundary of molecular nitrogen cg-N [12]. As pointed out previously[13], the predicted [7] transition pressure (50 ± 15 GPa) for the formation of polymeric cg-N from molecular nitrogen falls within the region of metastability, cg-N will persist at low pressures and temperatures. Compared to the simple cubic (sc) structure which was found to be mechanically unstable over the entire pressure range considered, the cg structure was found to be metastable over a pressure range up to 360 GPa [13]. Experimentally, by the x-ray diffraction of nitrogen at pressures up to 170 GPa it has been pointed out that the transformation of the diatomic phase into the single-bonded(polymeric) phase, which is the cg-N structure proceeds as a first order transition with the volume change [4]. Also, by the x-ray diffraction, it has been shown that the amorphous nature of the semiconducting nonmolecular material transforms to the crystalline cg-N phase on heating above 2000K, this indicates a sequence of transitions associated with the molecular to atomic transition of solid nitrogen [14].

Regarding the thermodynamic properties of the cg- N high-pressure phase diagram of nitrogen has been calculated [15]. This connects the observed molecular to cg-N polymer phase transition in the solid at 110GPa, to a liquid-polymer phase line which was obtained from the shock cooling measurements. For the polymeric structures of nitrogen(cg-N), calculation of the variation of enthalpy with the pressure up to 90 GPa [6]and 400 GPa[16] has been reported. Also, the coexistence line of molecular and polymeric cg-N has been predicted and, the phase transition parameters, latent heat, volume and entropy jumps have been calculated [17].

*Corresponding Author

Table 1. Values of the coefficients for the volume V(T) and for the bulk modulus B(T) according to Eqs.(1) and (6), which were fitted to the thermal expansivity V_0(T) and the bulk modulus K_0 (T) data [18], respectively, at P=0 for the cg-N, as also given in our previous study[20].

V(T) (Å^3)	V_0 (Å^3)	$-\alpha x10^{-6}$ (Å^3/K)	$\beta x10^{-7}$ (Å^3/K^2)	B(T) (GPa)	κ_0 (GPa)	$-\alpha' x10^{-3}$ (GPa/K)	$-\beta' x10^{-5}$ (GPa/K^2)
Eq.(1)	52.47	4.73	7.63	Eq.(6)	298.28	9.1	1.3

Regarding more recent studies on the cg-N structure, unusual high- pressure cg-N was experimentally synthesized and the first-principle calculations were performed [21]. Molecular and polymeric cg has been predicted by the equations of state, and the phase transition parameters (latent heat, volume and entropy) were calculated [22]. In relation to the cg-N structure, another nitrogen-based solid of N_8 molecular crystal (stable at ambient pressure) has been predicted [23]. Several phases of nitrogen including highly energetic phase, covalently bound cg-N have been studied by density functional theory (DFT)[24].Polymeric cg-N phase has been studied by the molecular dynamics and metadynamic simulations [25]. Also, using the first-principle calculations the thermodynamic and kinetic stabilities in polymorphs and cg-N have been investigated [26]. Experimentally, x-ray diffraction measurements of nitrogen also for the cg covalent solid have been performed [27]. Using DFT, single-bonded 3D nitrogen allotrope (cg-N) has been studied [28]. Experimentally study on the phase transition from cg-N to LPN (post-layered polymeric nitrogen) has been reported [29]. Very recently, solid nitrogen and nitrogen- rich compounds [30], cg phase in highly compressed nitrogen solid has been studied [31].

Over the years, various aspects of the cg-N have been studied both experimentally and theoretically as stated above. However, the thermodynamic properties of the cg-N structure have been explained to some extend in some earlier studies as stated above, when compared to the well-known solid phases (α,β,γ at low temperatures and ε, δ, υ, ξ at high pressures) of N_2 in the P-T phase diagram [10]. This has motivated us to study the cg-N phase exhibiting interesting features regarding its thermodynamic quantities which differ from those in the solid phases of N_2. From this point of view, by using some literature data, those thermodynamic quantities of interest are calculated at various temperatures and pressures for the cg-N structure. Regarding some earlier studies [18,20], the present work gives the calculation method of those thermodynamic quantities at higher pressures as well as their temperature dependence at zero pressure in the cg-N structure. Considering the pressure effects which changes the critical behavior of those thermodynamic quantities (mainly κ_T, α_p and B) at various temperatures in the cg-N phase, their pressure dependence has not been investigated extensively in the earlier works [18,20]. The pressure dependence as studied here, is also the principal improvement and contributions to the thermodynamic properties of the cg-N structure. For the high-pressure studies, it is important to achieve the cg-N structure as the most stable phase which has been obtained experimentally [2,12]. Thus, it was obtained experimentally that by the existence of the stable cg-N phase, the transition from the molecular phase to the polymeric form of nitrogen was realized. This states that investigation of the thermodynamic properties of the cg-N phase becomes important, particularly, at high pressures. This is the main objective of the present study. In particular, due to the literature data available our interest is focused on the calculation of the temperature and pressure dependence of the volume (V), thermal expansion (α_P), bulk modulus (B), isothermal compressibility (κ_T), specific heat (C_P) and the macroscopic Grüneisen parameter (γ) in the cg phase of nitrogen. For this calculation, the thermodynamic data obtained at constant pressures(0,35, 125 and 250 GPa) at 295 K [18] and for the V-P calculation (T=295 K) the experimental data [12] are used.

2. Calculation Methods

The temperature and pressure dependence of the volume for the cg-N was analyzed by using the thermodynamic data to calculate the thermodynamic quantities in this system. Our hypothesis for this calculation was to write the temperature and pressure dependence of the volume for the cg-N phase in the simplest functional form in order to explain the experimental measurements of V(T) and V(P). Therefore, they were expressed in the quadratic form. Also, our hypothesis was to use the quadratic form for the other thermodynamic quantities, namely, bulk modulus B(T) and heat capacity C_v(T) to describe the cg-N phase

2.1 Temperature dependence of the thermodynamic quantities

The temperature dependence of the volume for the cg-N can be analyzed at constant pressures according to

$$V(T) = V_0 + \alpha T + \beta T^2 \tag{1}$$

where V_0 , α and β are constants. In Eq.(1), those constants represent nonlinear variation of the volume with the temperature (in the quadratic form). So that V_0 is the volume at the absolute temperature(T=0), α and β are the linear and nonlinear (quadratic) variations of the volume with the temperature, respectively (α is the volume per degree and β is the volume per degree squared). By means of the definition of the thermal expansion, in thermodynamics as $\alpha_P \equiv (1/V)\,(\partial V/\partial T)_P$, its temperature dependence is obtained from Eq.(1),

$$\alpha_P = \frac{\alpha + 2\beta T}{V_0 + \alpha T + \beta T^2} \tag{2}$$

Also, the temperature dependence of the isothermal compressibility κ_T can be obtained from the definition of the slope dP/dT of the transition line in the P-T phase diagram for the cg-N in the polymeric phase using the thermodynamic identity

$$dP/dT = \alpha_P/\kappa_T \tag{3}$$

By knowing the V, α_P and κ_T ,the temperature dependence of the heat capacity C_P can be obtained through the thermodynamic relation,

$$C_P = C_V + TV\,({\alpha_P}^2/\kappa_T) \tag{4}$$

This gives rise to the macroscopic Grüneisen parameter by the definition in the thermodynamics as

$$\gamma = (V/C_V)(\alpha_P/\kappa_T) \tag{5}$$

The temperature dependence of the isothermalcompressibility K_T (=1/B) which is the inverse bulk modulus B and the temperature dependence of the specific heat C_V can be analyzed by expressing

$$B(T) = \kappa_0 + \alpha' T + \beta' T^2 \tag{6}$$

And

$$C_V(T) = e_0 + e_1 T + e_2 T^2 \tag{7}$$

respectively, where $\kappa_0, \alpha', \beta'$ and e_0, e_1, e_2 are constants. In Eq.(6), the constants κ_0 defines the bulk modulus B(T) at the absolute zero(T=0), the coefficients α' and β' represent per unit degree (linear variation) and B(T) per unit degree squared (quadratic variation), respectively. Similarly, for the heat capacity $C_v(T)$ in Eq.(7), e_0 is the C_v at T=0, e_1 and e_2 are the coefficients of the C_v per degree and per degree squared, respectively, as for the nonlinear terms of V(T) (Eq.1) and B(T) (Eq.6). On the basis of the experimental measurements of the V(T), α_p(T), dP/dT, C_p(T) and B(T) through the expressions (Eq. 1,2,3,4 and 6), those constants and variables become significant, and they need to be determined. The temperature dependence of the C_p, isothermal bulk modulus K(T) and thermal expansion α(T) have been given in the polynomial form for the melting of β-quartz previously [32]. However, their expressions for those thermodynamic quantities include terms such as T^{-1}, T^{-2} etc., which characterize rather different behavior for melting. We have given our relations (Eqs. 1,6 and 7) with the thermodynamic relations (Eq.4) for the cg-N phase in our earlier study [20].

2.2 Pressure dependence of the thermodynamic quantities

Pressure dependence of the thermodynamic quantities can also be analyzed for the cg-N at room temperature. As we stated for the V(T), B(T) and C_v, the pressure dependence of V(P) and k_T , our hypothesis was to express them in the simplest functional form. Thus, by writing the V(P) in quadratic form, the pressure dependence of the α_p, C_p and γ were obtained in order to describe the experimental measurements of those quantities accordingly n the cg-N phase. We have also given Eqs.(8) and (11) for the cg-N structure in our previous study [20]. Volume can be expressed as a function of pressure as

$$V(P) = b_0 + b_1 P + b_2 P^2 \tag{8}$$

where b_0, b_1 and b_2 are constants. In this equation, the coefficient b_0 is the volume at zero pressure (P=0), b_1 and b_2 are the volume per unit pressure and the square of the pressure, respectively. Those constants (b_0, b_1 and b_2) are also significant as determined from the V-P measurements in the cg-N structure. Thus, from the V-T measurements through Eq.(1) and also using V(P) relation (Eq.8) the P-T phase diagram with the slope dP/dT (Eq.3) can be determined in the cg-N phase. Thus, from Eq.(8) the isothermal compressibility κ_T can be obtained by using the definition $\kappa_T \equiv (-1/V)\,(\partial V/\partial P)_T$ as

3. Results

For the temperature dependence of the thermodynamic quantities, the volume was first analyzed according to Eq.(1), as also analyzed previously with the values given [18] at

$$\kappa_T = -\frac{b_1 + 2b_2 P}{b_0 + b_1 P + b_2 P^2} \tag{9}$$

Also through Eq.(3), the pressure dependence of the thermal expansion can be written as

$$\alpha_P = -(dP/dT)\left(\frac{b_1 + 2b_2 P}{b_0 + b_1 P + b_2 P^2}\right) \tag{10}$$

This provides the pressure dependence of C_P-C_V according to the thermodynamic relation (Eq.4). Finally, by knowing the pressure dependence of those quantities Eq.(4), macroscopic Grüneisen parameter (γ) can be calculated at various pressures (Eq.5).

Table 2. Values of the thermal expansion (α_p),bulk modulus (B), the slope dP/dT in the P-T phase diagram and the macroscopic Grüneisen parameter γ at T=295 K (P=0) for the cg-N. We also give the values of the volume V calculated from the equations indicated at constant pressures (T= 295 K).

P=0	α_px10^{-5} (K^{-1})	B (GPa)	(dP/dT)x10^{-3} (GPa/K)	γ	T= 295 K	V(Å^3) P=0	V(Å^3) P=35 GPa	V(Å^3) P=125 GPa
T=295 K	0.81	294.46	2.385	3.35	Eq.(1)	7.44	6.00	5.54
					Eq.(8)	6.77	6.08	5.14

Table 3 Values of the coefficients e_0, e_1 and e_2 for the specific heat C_V(T) according to Eq.(7) which was fitted to the C_V-T data [18] at the pressures indicated for the cg-N.

P (GPa)	$-e_0$ (J/mol.K)	e_1 (J/mol.K^2)	$-e_2$x10^5 (J/mol.K^3)
0	18.72	0.16	5.77
5	18.41	0.18	7.72
25	19.06	0.21	10.3
50	16.59	0.22	11.9

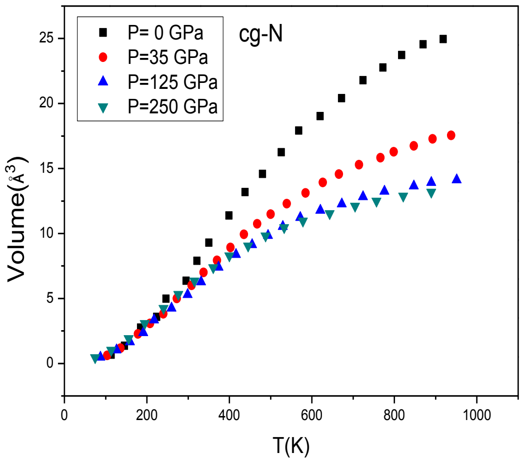

Figure 1 Volume as a function of temperature according to Eq.(5) through Eq.(3) using the C_v data [18] for the cg-N.

various temperatures (P=0) for the cg-N. For this analysis and in the simulations, we used the computer programme of OriginLab. Values of the coefficients of V(T) are given in Table 1, as also given in our previous study [20]. The temperature dependence of the bulk modulus (B) (=1/κ_T) was then analyzed according to Eq.(6) as also analyzed in our previous work [20] by using the bulk modulus K_0 data [18] (P=0) with the coefficients determined (Table 1) in the cg-N phase. This provided us to determine the slope value of dP/dT (Eq.3) in the P-T phase diagram of the cg-N phase by using the values of α_P and B at P=0, T=295 K. The values of the thermal expansion α_P , bulk modulus B and the dP/dT value at T=295 K (P=0) are given in Table 2. By analyzing the C_V(T) data [18] at P= 0 according to Eq.(7), the coefficients e_0, e_1 and e_2 , were determined, as given in Table 3. Also, by analyzing the V(P) data [12] at T=295 K according to Eq.(8) the values of b_0, b_1 and b_2 were obtained. (Table 4). This enabled us to evaluate the macroscopic Grüneisen parameter γ (Eq.5) by using the values of V(=b$_0$), C_V and dP/dT (Table 2) at P=0 (T=295 K), which we is given in Table 2.

At constant pressures of 35, 125 and 250 GPa, the γ values were also evaluated(Eq.5) by using the V(P) [12] and the C_V data [18] with constant dP/dT value (Table 2). For this calculation, the C_V data were analyzed according to Eq.(7) for the pressures considered with the coefficients of e_0, e_1 and e_2 which were determined , as given in Table 3. By means of the γ values determined, the temperature dependence of the volume V(T) was then calculated using the C_V data with the constant dP/dT (Table 2) at the pressures of 0, 35, 125 and 250 GPa, as plotted in Figure 1. Values of the coefficients for V(T) for constant pressures studied according to Eq.(1), are given in Table 5. From the temperature dependence of the volume V(T) (Figure 1), the thermal expansion α_P was obtained according to Eq.(2) as a function of temperature at the pressures of 0, 35, 125 and 250 GPa, as plotted in Figure 2. This also gave us the temperature dependence of the isothermal compressibility κ_T (Eq.3) where dP/dT value (Table 2) was used, and the bulk modulus B(T) was obtained at constant pressures, as plotted in Figures 3 and 4, respectively. By knowing the temperature dependence of V(T), α_P and κ_T (Eq.3) and using the C_V(T) data , the specific heat C_p was then predicted at constant pressures of 0, 35, 125 and 250 GPa according to Eq.(4) for the cg-N, as plotted in Figure 5.

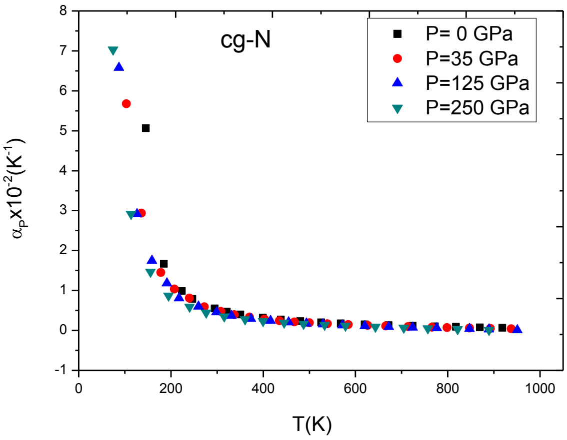

Figure 2 Thermal expansion α_P as a function of temperature (Eq.2) at the pressures indicated for the cg-N.

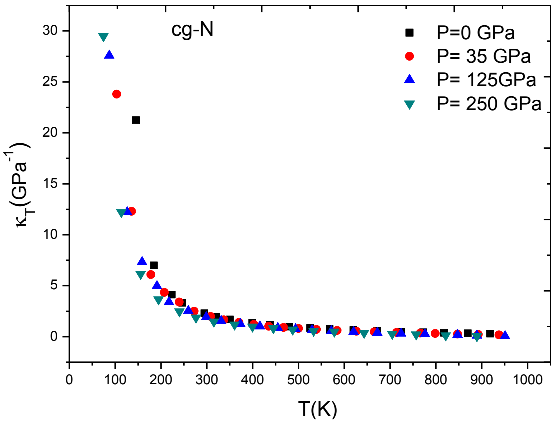

Figure 3 Isothermal compressibility κ_T as a function of temperature (Eq.3) at constant pressures indicated for the cg-N.

Regarding the pressure dependence of the thermodynamic quantities for the isothermal compressibility of the cubic structure a/a$_0$ lattice parameter data [18] were used at various pressures (at T=295 K) for κ_T as defined above with the a/a$_0$ using

$$\kappa_T/\kappa_0 = b_0' + b_1'P + b_2'P^2 \qquad (11)$$

where b_0', b_1' and b_2' are constants, the pressure dependence of the volume can be then calculated according to

$$lnV(P) = -\int_0^{P_0} b_0'\,dP - \int_0^{P_0} b_1'\,PdP - \int_0^{P_0} b_2'\,P^2dP \qquad (12)$$

Table 4 Values of the coefficients b_0, b_1 and b_2 of the volume V(P) which was fitted to the V-P data [12] at T=295 K according to Eq.(8). The coeffcients b_0', b_1' and b_2' of the isothermal compressibility κ_T/κ_0 (normolized) were obtained by fitting Eq.(11) to the lattice parameter a/a₀ data [18] at T=295 K for the cg-N.

V(P) (Å^3)	b_0 (Å^3)	$-b_1$x10^{-2} (Å^3/GPa)	b_2x10^{-5} (Å^3/ GPa^2)	κ_T/κ_0	b_0'	$-b_1'$x10^{-4} (GPa^{-1})	b_2'x10^{-6} (GPa^{-2})
Eq.(8)	6.77	2.22	7.35	Eq.(11)	0.99	7.4	1.06

where P_0=250 GPa. The lattice parameter (a/a$_0$) data were then analyzed for the normalized κ_T/κ_0 with the coefficients determined (Table 4), as also given in our previous work [20]. In Figure 6, the volume V(P) deduced from κ_T/κ_0(Eq.11) is plotted according to Eq.(12) with the observed V-P data [12] at 295 K. With the constant dP/dT value (Table 2), the pressure dependence of the thermal expansion α_P (Eq.3), and the bulk modulus B were obtained. α_P and κ_T are plotted as a function of pressure (T=295 K) in Figures 7 and 8, respectively. Similarly, from the pressure dependence of V, α_P, κ_T and the C_V data, the specific heat C_P was calculated (Eq.4) at constant pressures of 0,35,125 and 250 GPa, as plotted in Figure 9. Finally, the macroscopic Grüneisen parameter γ was calculated at those constant pressures according to Eq.(5) using the calculated values of V, α_P, κ_T and the C_V data , as plotted in Figure 10. Note that for the analysis of the B(T) (Eq.6), C_V(T)(Eq.7), V(P) (Eq.8) and κ_T/κ_0(Eq.11), we also used the programme (OriginLab) in our simulations.

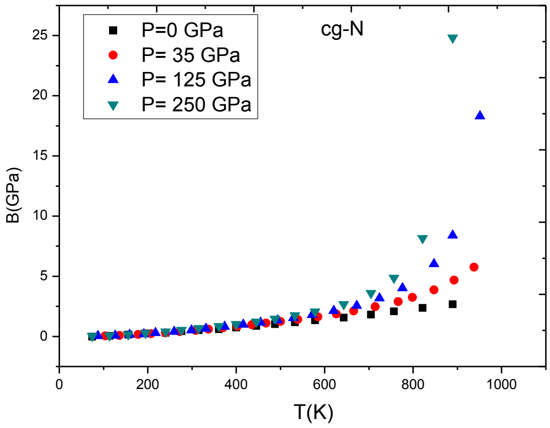

Figure 4 Bulk modulus B(T) as a function of temperature according to B(T)=1/κ_T (Eq.3) at the pressures indicated for the cg-N.

4.Discussion

Volume V(T) which was calculated at various temperatures, decreases as the pressure increases for the cg-N (Figure 1). Pressure effects considerably from 0 to 35 GPa, whereas its effect becomes insignificant above 125 GPa for the cg-N. Above the room temperature (T=295 K), the volume values are separated considerably as the pressure increases up to 125 GPa (Figure 1). The temperature dependence of the thermal expansion α_P(Figure 2) and isothermal compressibility κ_T (Figure 3)at the pressures of 35 ,125 and 250 GPa, exhibit similar critical behavior as in the zero pressure for the cg-N. They decrease as the temperature increases up to 1000K. An abrupt decrease in the α_P and κ_T occurs just above about 100K in the cg-N at constant pressures indicated (Figures 2 and 3). Since a constant slope value of dP/dT (Table 2) was considered in the P-T phase diagram of the cg-N according to Eq.(3), the same critical behavior was obtained at the pressures of 0, 35, 125 and 250 GPa as expected. As shown in Figures 2 and 3, calculated α_P and κ_T, decreasing with increasing temperature exhibit similar critical behavior which is independent of the pressures (0, 35, 125 and 250 GPa) for cg-N. This is also expected since the temperature increases the volume and it decreases the compressibility of the structure in the cg phase of nitrogen, as also indicated previously [18].Also, at ambient pressure and low temperature nitrogen freezes into a diatomic solid where strongly covalent (N≡N) N_2 molecules are weakly (van der Waals) bonded to each other as stated in an earlier study[13]. On the other hand, the bulk modulus B and the specific heat capacity C_P increase as the temperature increases as shown in Figures. 4 and 5, respectively. An abrupt increase of B occurs at about 900 K (Figure 4). The pressure does not effect on the B(T) up to about 600 K above which the diverging behavior seems to occur with the larger values as the pressure increases (Figure 4). Instead of anomalous behavior of the α_P (Figure 2) and κ_T (Figure 3) and B (Figure 4), the heat capacity C_p increases monotonically as the temperature increases with the larger C_p values at higher pressures (Figure 5).

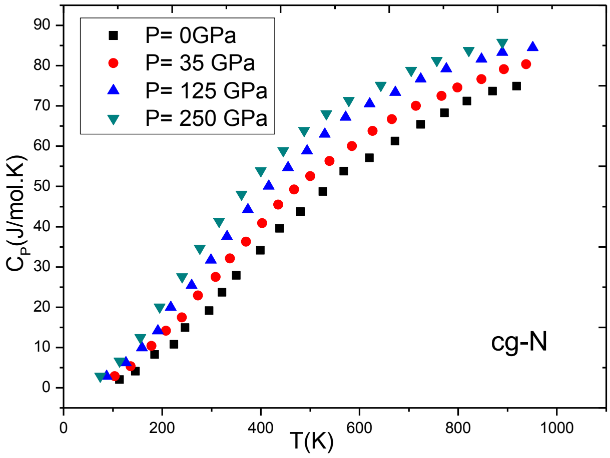

Figure 5 The specific heat as a function of temperature (Eq.4) by using the V(T) values (in this study) and the C_V(T) data[18] at the pressures indicated for the cg-N.

Our value of dP/dT= 2.385x10^{-3} GPa/K for the cg-N which we obtained, can be compared with the experimental value of dT$_m$/dP=35K/GPa or dP/dT$_m$=0.029 GPa/K up to 50 GPa for the melting temperature of the solid-liquid transition in nitrogen [33]. We see that our calculated value of dP/dT for the cg-N phase is much smaller (one order of magnitude) than the experimental value of the melting point in nitrogen.

Regarding the pressure dependence of the volume V (Figure 6), κ_T/κ_0(Figure 7), α_P(Figure 8), and γ (Figure 10), calculations indicate that they decrease whereas C_P (Figure 9) increases with the pressure increasing from 0 to 250 GPa at T=295 K in the cg-N. As pointed out previously [18] under the compression, crystalline atomic structure develops and the formation of nonmolecular single bonded polymorphs involves the dissociation of the extremely strong triple N≡N bond into three weaker single N-N bonds [12]. This is in accordance with the theory which predicts dissociation of the molecule and formation of monatomic phases similar to those observed in group V elements such as phosphorus and arsenic, as also pointed out in an earlier study [13]. At extremely high pressures nitrogen is predicted to occur in the simple cubic structure instead of cg-N structure[13]. Since the α_P, κ_T , C_P and γ were calculated by using the C_V data at constant pressures of 0,35,125 and 250 GPa (T=295K), plots (Figures 7-10) were restricted to the four data points only, which still give the general trend. As seen from Figure 6, the volume calculated (Eq.12) as a function of pressure at T= 295 K agrees with the observed data [12]. In this plot, the curve represents the best fit to the experimental data according to Eq.(8) with the coefficients determined (Table 4). Note that in Figure 7, the isothermal compressibility κ_T was normalized (κ_T/κ_0) since the κ_T was analyzed by using the normalized lattice parameter data normalized (a/a_0)[18] for the cg-N at 295 K. As in the case of the normalized isothermal compressibility (Figure 7), the pressure dependence of the α_P(Figure 8) and C_P (Figure 9) can be compared when the measured thermodynamic data become available in the literature for the cg-N. This examines whether our calculated thermodynamic quantities (κ_T/κ_0, α_P, and C_p) at various pressures (T=295 K) for the cg-N structure are adequate which also validate our simulations procedure. For the calculation of κ_T/κ_0, α_P, and C_p, we started with the V(P) relation (Eq.12) which was fitted to the observed volume data [12) satisfactorily (Figure 6). On the basis of the experimental data as our reference, decreasing κ_T/κ_0,(Figure 7) and α_P (Figure 8), and increasing C_p (Figure 9) with the increasing pressure (T= 295 K) are then expected for the cg-N. Regarding the temperature dependence of the thermodynamic quantities, we started with the calculation of V(T) at constant pressures(0, 35,125, 250 GPa), as plotted in Figure 1. The V(T) calculation was also based on the experimental V(P) data [12] which were fitted (Eq.8) as stated above (Figure 6). By obtaining the temperature dependence of the thermodynamic quantities (C_v, α_P, κ_T and γ) , V(T) was calculated through Eq.(5) at constant pressures studied as plotted in Figure 1. The calculated volume V(T=295 K) at P=0, 35 and 125 GPa (Figure 1) can be compared with those V(P) at T=295 K (Figure 6). They were deduced from Eqs. (1) and (8) with the values in Tables 5 and 4, respectively, as given in Table 2. Those volume values are comparatively close to each other with the errors of 0.67 (P=0), 0.08 (P= 35 GPa) and 0.39 Å^3 (P=125 GPa). This small discrepancy between our calculated V(T) values at constant pressures (0, 35,125 and 250 GPa) and the observed V(P) data (T=295 K) [12], as shown Figures. 1 and 6, respectively, indicates that our results are validated for the cg-N structure.

Regarding the temperature dependence of α_P, κ_T, B and C_p, as plotted in Figures 2,3,4 and 5, respectively, they were originally extracted from the V(T) which was calculated at constant pressures studied (Figure 1), as stated above. Because of the fact that our calculated V(T) at P=0 (Figure 1) agrees with the observed V(P) at T= 295 K (Figure 6), predicted values of those thermodynamic (α_P, κ_T, B and C_p) should be acceptable at P=0. At higher pressures (35,125 and 250 GPa), our calculated values should also be reasonably well as compared with the experimental measurements for the cg-N structure when available in the literature. Our predictions are therefore important in the sense that they give an initiative for the experimental measurements to describe the cg-N structure thermodynamically.

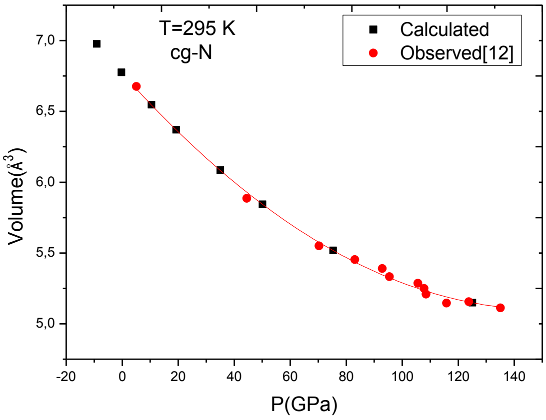

Figure 6 Volume V(P) at various pressures (Eq.12) using the (a/a_0) lattice parameter data [18] for the cg-N (T= 295 K). Solid line represents the best fit to the observed data [12] as shown (Eq.8) with the coefficients determined (Table 4).

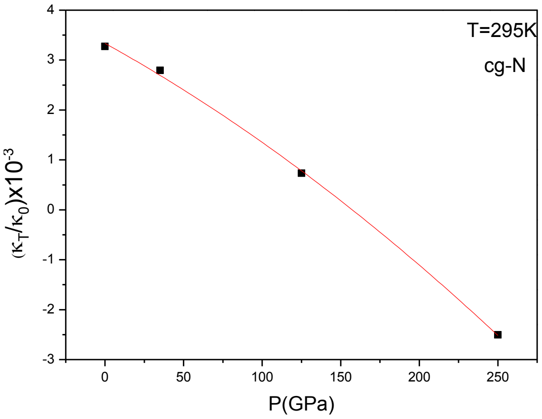

Figure 7 The isothermal compressibility κ_T/κ_0 (normalized) as a function of pressure (T=295 K) according to Eq.(11) for the cg-N. Solid line represents the best fit to the κ_T/κ_0 values with the coefficients determined (Table 4).

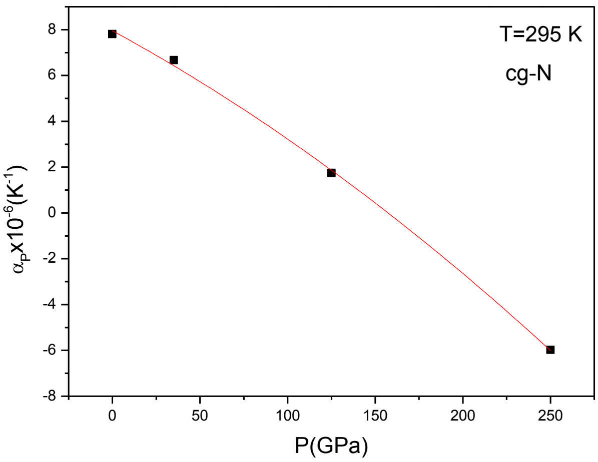

Figure 8 Thermal expansion α_p as a function of pressure (T=295 K) according to Eq.(3) from the normalized isothermal compressibility κ_T/κ_0 for the cg-N. Solid line represents the best fit to α_p values.

As mentioned above for the V(P) at T=295 K (Figure 6), our fit (Eq.8) to the observed data [12] is reasonably good. Similar fit was conducted for the powder and single crystal of the cg-N structure by using the Birch-Murnaghan (BM) equation of state (EOS) [12]. This shows that our V(P) calculation on the basis of the P-V measurements, can be compared with the Birch-Murnaghan EOS for the cg-N structure.

On the basis of the V(P) fit to the experimental data (Figure 6), the pressures dependences of κ_T/κ_0 (Figure 7), α_P(Figure 8), C_P (Figure 9) and γ (Figure 10), which we predicted for the cg-N structure, are expected to agree with the experimental measurements (the macroscopic Grüneisen parameter should be calculated from the measured V, C_p, α_P, κ_T according to Eq.5) when available in the literature, as stated above.

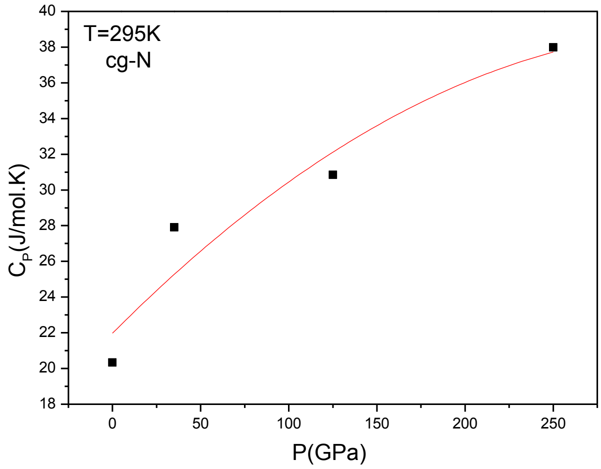

Figure 9 Specific heat C_P calculated as a function of pressure at T=295 K (Eq.4) using the C_V data [18] for the cg-N. Solid line represents the best fit to the C_P values (Eq.4).

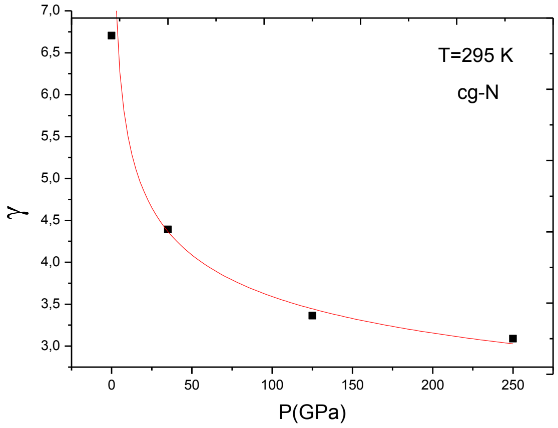

Figure 10 Macroscopic Grüneisen parameter as a function of pressure (Eq.5) using the C_V-P data [18] at T=295 K for the cg-N.

5.Conclusions

Temperature dependence of the thermodynamic quantities the volume (V), thermal expansion (α_P), isothermal compressibility (κ_T) bulk modulus (B), heat capacity (C_P) and the macroscopic Grüneisen parameter (γ) were calculated at constant pressures (0,35,125 and 250 GPa) for the cg-N. The pressure dependences of the κ_T, α_P and C_p and γ were also calculated at room temperature (T=295 K) for this structure. By assuming the polynomial (quadratic) form of V(T) and V(P), those calculations were performed through the thermodynamic relations using the thermodynamic data from the literature, in particular, for the V(T), B(T) at zero pressure and C_v(T) at constant pressures which were considered for the cg-N phase.

Our results show that the increase in the V(T) at the higher pressures, tends to lower as compared to the V(T) at P=0. Additionally, the temperature dependence of α_P and κ_T decreases anomalously starting from nearly T= 100 K at constant pressures studied. This indicates that the cg-N phase undergoes to a solid phase at low temperatures (below~100 K). Calculated thermodynamic quantities which were obtained in this study can be compared with the measured thermodynamic data for the cg-N when available in the literature.

As we started from the V(T) at zero pressure to calculate the temperature dependence of the thermodynamic quantities at constant pressures, which were presented in this study also by starting from the V(P) at room temperature, those thermodynamic quantities can be calculated at higher constant temperatures for the cg-N structure by the same calculation method given here. This can be considered as a future work for the cg-N phase. This method of calculating the thermodynamic quantities can be applied to some other structures.

Nomenclature

B	bulk modulus
C_p	heat capacity
C_v	specific heat capacity
K	bulk modulus
P	pressure
T	temperature
V	volume
κ_T	isothermal compressibility
α_P	thermal expansion
γ	macroscopic Grüneisen parameter

Greek letters

α , β, γ, ε, δ, υ, ξ	phases of solid nitrogen

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