

PIPPARD RELATIONS FOR CUBIC GAUCHE NITROGEN

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ABSTRACT

The Pippard relations (C_P vs. α_P and α_P vs. κ_T) are examined at various temperatures up to 1200 K at zero pressure ($P = 0$) for the cubic gauche nitrogen. The specific heat (C_P) is related to the thermal expansion (α_P) and the α_P is also related to the isothermal compressibility (κ_T) as the Pippard relations for this solid structure. For those relations, experimental data are used from the literature. It is found that the variation of the C_P with the α_P and α_P with the κ_T is linear. Using the linear relations dP/dT is predicted, which can be compared with the experimental measurements in the $P - T$ phase diagram of cubic gauche nitrogen.

Keywords: Pippard relations. Cubic gauche nitrogen

1. INTRODUCTION

Nitrogen exhibits a number of solid phases in the $P - T$ phase diagram [1-7]. Dissociation of the nitrogen molecules under pressure to form a polymeric phase has been studied both theoretically [8] and experimentally [6, 9] in nitrogen.

At higher pressures, structures of δ , δ_{loc} , ϵ and ζ occur [2, 3] in this solid crystal. It has been pointed out that a transition to nonmolecular (NM) phase also occurs in the 140 - 160 GPa range [10]. It has been proposed [11] that the covalent polymeric lattice should have an unusual cubic gauche (cg-N) structure, as the atomic single bonded nitrogen with this structure has been synthesized at high pressure of ~ 110 GPa and high temperature of ~ 2000 K [12, 13]. This has been studied theoretically using density functional methods [8, 11, 14] and observed experimentally [6, 9, 10, 12, 13]. The structure of the phase was found to be cubic gauche with its bulk modulus ≥ 300 GPa, characteristic of strong covalent solids [12]. The lattice dynamical properties of the cubic gauche phase of nitrogen have been computed using density functional theory and its structure has been found to be stable up to at least 250 GPa [15]. On the basis of the dynamical data, the thermodynamic properties have been derived [15].

In this study, we analyze the volume V , the bulk modulus B and the specific heat C_V as a function of temperature ($P = 0$) and, also compressibility K and the volume as a function of pressure for cubic gauche nitrogen using the literature data [15]. By calculating the temperature dependence of the thermal expansion and the specific heat through the thermodynamic relations, the Pippard relations are constructed for cubic gauche nitrogen.

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Below, in section 2 we give our analysis and results. In section 3, Pippard relations for cubic gauche nitrogen are given and they are discussed in section 4. Conclusions are given in section 5.

2. ANALYSIS AND RESULTS

2.1 Analysis of the Volume V(T) and the Bulk Modulus B(T) at P = 0

We obtained the temperature dependence of the volume for the cubic gauche nitrogen at ambient pressure [1] according to the quadratic function

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

where V_0 , α and β are constants. Their values are given in Table 1. Analysis of the temperature dependence of the bulk modulus B for the cubic gauche nitrogen [15] was performed here according to the relation

$$B(T) = \beta_0 + \alpha' T + \beta' T^2 \tag{2}$$

where β_0 , α' and β' are constants. Their values are given in Table 1.

Table 1. Values of the parameters (Eqs. 1 and 2) for the cubic gauche nitrogen using the values at ambient pressure [15]

V(T)	V_0 (Å ³)	$\alpha \times 10^{-5}$ (Å ³ /K)	$\beta \times 10^{-7}$ (Å ³ /K ²)	B(T)	β_0 (GPa)	$\alpha' \times 10^{-3}$ (GPa/K)	$\beta' \times 10^{-5}$ (GPa/K ²)
Eq. (1)	52.48	-4	7.9	Eq. (2)	298.28	-9.1	-1.3

2.2 Analysis of Compressibility K(P) and the Volume V(P)

Here we analyzed the pressure dependence of the compressibility of the cubic structure in nitrogen using the lattice parameter data (a/a_0) according to the polynomial

$$K(P) = b_0 + b_1 P + b_2 P^2 \tag{3}$$

where b_0 , b_1 and b_2 are constants. Their values are given in Table 2. We also analyzed the pressure dependence of volume using the lattice parameter data a (Å) [1] according to the relation

$$V(P) = c_0 + c_1 P + c_2 P^2 \tag{4}$$

where c_0 , c_1 and c_2 are constants (Table 2).

Table 2. Values of the fitted parameters according to (Eqs.3 and 4) for the cubic gauche nitrogen using the lattice parameter data (a/a_0 for the compressibility κ_T and a (Å) for the volume V) [15]

K(P)	b_0	$b_1 \times 10^{-4}$ (GPa ⁻¹)	$b_2 \times 10^{-6}$ (GPa ⁻²)	V(P)	c_0 (Å ³)	c_1 (Å ³ /GPa)	$c_2 \times 10^{-4}$ (Å ³ /GPa ²)
Eq.(3)	0.99	-7.4	1.06	Eq.(4)	54.487	-0.01	-8

2.3 Pippard Relations for Cubic Gauche Nitrogen

We examined the Pippard relations [16] for cubic gauche nitrogen according to

$$C_p = TV\alpha_p(dP/dT) + T(dS/dT) \quad (5)$$

and

$$\alpha_p = \kappa_T(dP/dT) + (1/V)(dV/dT) \quad (6)$$

where dP/dT is the slope of the P - T phase diagram of the cubic gauche nitrogen In Eq. (5), dS/dT denotes the change in the entropy S for this structure.

In order to establish the Pippard relations (Eqs. 5 and 6), we first calculated C_p using the thermodynamic relation

$$C_p = C_v + TV\alpha_p^2 \quad (7)$$

where we used the temperature dependence of the volume V (Eq. 1) and the thermal expansion α_p which was derived from Eq. (1) according to the definition $\alpha_p = (1/V)(\partial V/\partial T)_P$

$$\alpha_p(T) = d_0 + d_1T + d_2T^2 \quad (8)$$

The values of the parameters d_0 , d_1 and d_2 are given in Table 3.

Table 3. Values of the coefficients for the $\alpha_p(T)$ and $C_v(T)$ according to the Eqs. (8) and (9) respectively, for cubic gauche nitrogen

$\alpha_p(T)$ (K ⁻¹)	$d_0 \times 10^{-4}$ (K ⁻¹)	$d_1 \times 10^{-7}$ (K ⁻²)	$d_2 \times 10^{-9}$ (K ⁻³)	$C_v(T)$ (J/mol.K)	e_0 (J/mol.K)	e_1 (J/mol.K ²)	$e_2 \times 10^{-5}$ (J/mol.K ³)
Eq.(8)	3.98	5.16	1.4	Eq.(9)	-21.4	0.171	7.14

The C_v values were obtained for the cubic gauche structure of nitrogen as a function of temperature at zero pressure (P = 0) according to

$$C_v(T) = e_0 + e_1T + e_2T^2 \quad (9)$$

with the values of e_0 , e_1 and e_2 (Table 3).

Once we calculated the specific heat C_p (Eq. 7), we then examined the first Pippard relation (Eq. 5) by plotting C_p/T against $V\alpha_p$ as shown in Figure 1. The best fit (C_p/T vs. $V\alpha_p$) was obtained as a straight line according to Eq. (5) with the values of dP/dT and dS/dT within the temperature interval studied (Table 4).

Finally, we examined the second Pippard relation (Eq.6) by plotting the thermal expansion (α_p) as a function of the isothermal compressibility (κ_T) in values in Figure 2. We give the values of the slope (dP/dT) and the intercept $(1/V)(dV/dT)$, which we extracted in Table 4.

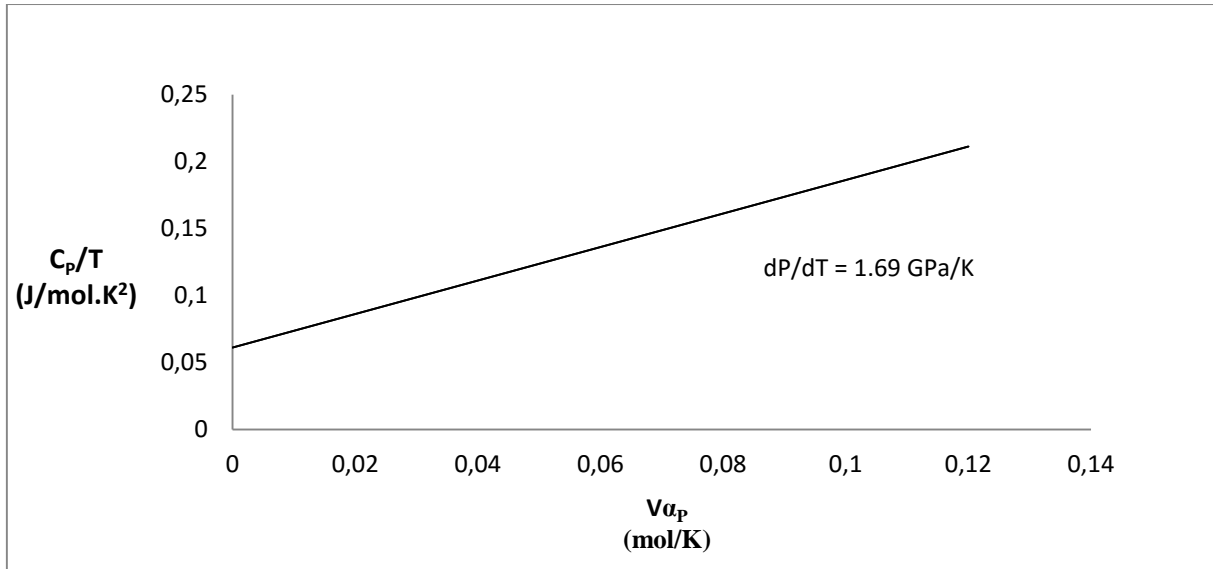


Figure 1. The first Pippard relation (Eq. 5) at various temperatures ($P = 0$) for cubic gauche nitrogen

Table 4. Values of the slope (dP/dT) and the intercepts according to the Pippard relations indicated for cubic gauche nitrogen

Pippard Relations	dP/dT (GPa/K)	$dS/dT \times 10^{-2}$ (J/mol.K ²)	$(1/V) (dV/dT)$ (K ⁻¹)	Temperature Interval (K)
Eq.(5)	1.69	1.4	-	0 < T < 1000
Eq.(6)	0.54	-	-0.526	

3. DISCUSSION

We examined here the Pippard relations (Eqs.5 and 6) by calculating the temperature dependence of the thermal expansion α_P , isothermal compressibility κ_T , and the specific heat C_P using the volume V and the specific heat C_V data [15] for cubic gauche nitrogen. We obtained linear plots of C_P/T vs. $V\alpha_P$ (Figure 1) and α_P vs. κ_T (Figure 2) at various temperatures ($P = 0$), as expected from the Pippard relations (Eqs. 5 and 6). The values of the slope dP/dT were extracted, which were 1.25 GPa/K (C_P/T vs. $V\alpha_P$) and 0.54 GPa/K (α_P vs. κ_T), as also given in Table 4. In principle, the dP/dT values should be the same. However, the data (C_V and V) [15] we used for our calculations, were obtained from the density functional theory which is based on some assumptions. Our calculated thermodynamic quantities can be compared with their experimental measurements and also pressure versus temperature measurements in the $P - T$ phase diagram for cubic gauche nitrogen under the given temperature and pressure conditions. This then provides the dP/dT values, which can then be compared with our dP/dT values (Table 4). Also, the Pippard relations can be examined at higher pressures such as $P = 35, 125$ and 250 GPa with the C_V values obtained [15] when the volume data are available at those constant pressures.

In regard to the nature of the cubic gauche structure in nitrogen, experimental studies [12, 13] lead to the formation of this structure passed through the amorphous state, as stated previously [15]. The transition to the polymeric nitrogen may be by passing through different molecular structures according to the thermodynamic stability fields [15, 17]. Elastic and vibrational properties of cubic gauche nitrogen [18-20] have confirmed the stability and highly energetic character of this phase under high pressures, as also pointed out previously [15].

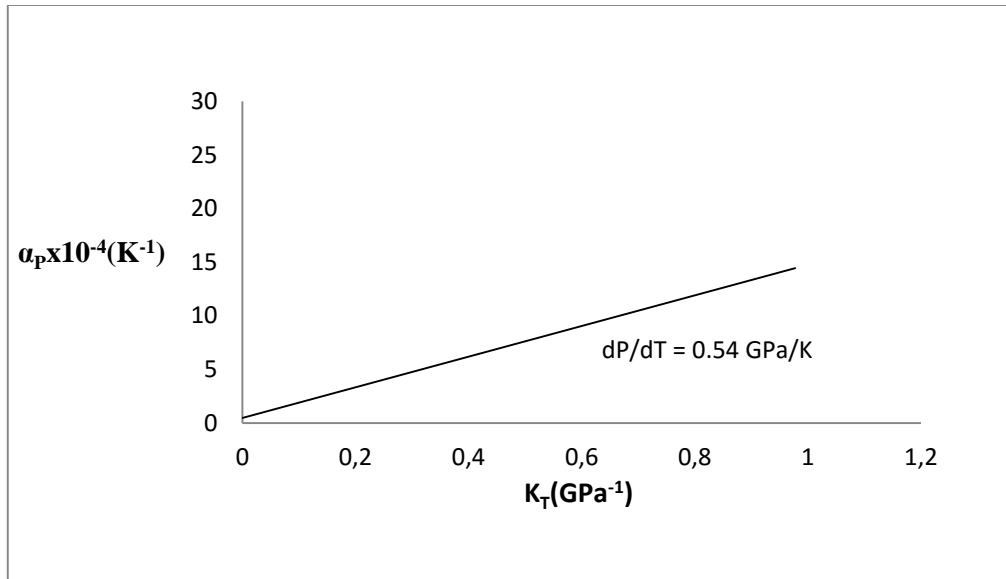


Figure 2. The second Pippard relation (Eq. 6) at various temperatures ($P = 0$) for cubic gauche nitrogen

4. CONCLUSIONS

The temperature dependence of the volume V , the bulk modulus B and the specific heat C_V and, the pressure dependence of the volume and compressibility κ_T were analyzed for the cubic gauche nitrogen using the data from the literature. On this basis, the thermal expansion α_P and the specific heat C_P were calculated as a function of temperature for this cubic phase of N_2 . The Pippard relations were examined at various temperatures ($P = 0$) which give linear variations of C_P with α_P and α_P with κ_T for the cubic gauche nitrogen (cg- N) as expected. The slope values of dP/dT were deduced from the Pippard relations, which are reasonable for this crystal structure. The Pippard relations can also be examined at various pressures at constant temperatures ($T = 293$ K) for cg- N .

REFERENCES

- [1] Schuch AF, Mills RI. Crystal structures of the three modifications of nitrogen 14 and nitrogen 15 at high pressure. *J Chem Phys* 1970; 52: 6000.
- [2] Lesar R, Ekberg S, Jones L, Mills R. Raman spectroscopy of solid nitrogen up to 374 kbar. *Solid State Commun* 1979; 32: 131.
- [3] Mills RL, Olinger B, Cromer DT. Structures and phase diagrams of N_2 and CO to 13 GPa by X-ray diffraction. *J Chem Phys* 1986; 84: 2837.
- [4] Belak J, Lesar R, Eters RD. Calculated thermodynamic properties and phase transitions of solid N_2 at temperatures $0 \leq T \leq 300$ K and pressures $0 \leq P \leq 100$ GPa. *J Chem Phys* 1990; 92: 5430.
- [5] Schneider H, Hafner W, Wokaun A, Olijnyk H. Room temperature Raman scattering studies of external and internal modes of solid nitrogen at pressures $8 \leq P \leq 54$ GPa. *J Chem Phys* 1992; 96: 8046.

- [6] Gregoryanz E, Goncharov AF, Hemley RJ, Mao HK, Somayazulu M, Shen G. Raman, infrared and X-ray evidence for new phases of nitrogen at high pressures and temperatures. *Phys Rev B* 2002; 66: 224108.
- [7] Mukherjee GD, Boehler R. High-pressure melting curve of nitrogen and the liquid-liquid phase transition. *Phys Rev Lett* 2007; 99: 225701.
- [8] McMahan AK, Lesar R. Pressure dissociation of solid nitrogen under 1Mbar. *Phys Rev Lett* 1985; 54: 1929.
- [9] Gregoryanz E, Goncharov AF, Hemley RJ, Mao HK. High pressure amorphous nitrogen. *Phys Rev B* 2001; 64: 052103.
- [10] Goncharov AF, Gregoryanz E, Mao HK, Liu Z, Hemley RJ. Optical evidence for a nonmolecular phase of nitrogen above 150 GPa. *Phys Rev Lett* 2000; 85: 1262.
- [11] Mailhot C, Yang LH, McMahan AK. Polymeric nitrogen. *PhysRev B* 1992; 46: 14419.
- [12] Eremets MI, Gavriiliuk AG, Trojan IA, Dzivenko DA, Boehler R. Single-bonded cubic form of nitrogen. *Nature Mater* 2004; 3: 558.
- [13] Eremets MI, Gavriiliuk AG, Trojan IA. Single –crystalline polymeric nitrogen. *App Phys Lett* 2007; 90: 171904.
- [14] Martin RM, Needs RJ. Theoretical study of the molecular-to-non molecular transformation of nitrogen at high pressures. *Phys Rev B* 1986; 34: 5082.
- [15] Caracas R. Raman spectra and lattice Dynamics of cubic gauche nitrogen. *J Chem Phys* 2007; 127: 144510.
- [16] Pippard AB. *The Elements of Classical Thermodynamics*, Cambridge University Press, Newyork, 1957.
- [17] Caracas R, Hemley RJ. New structures of dense nitrogen: path ways to the polymeric phase. *Chem Phys Lett* 2007; 442: 65.
- [18] Nordlund K, Krashennnikov A, Juslin N, Nord J, Albe K. Structure and stability of non-molecular nitrogen at ambient pressure. *Europhys Lett* 2004; 65: 400.
- [19] Zhang T, Zhang S, Chen Q, Pheng LM. Metastability of single-bonded cubic gauche structure of N under ambient pressure. *Phys Rev B* 2006; 73: 094105.
- [20] Yu HL, Yang GW, Yan XH, Xiao Y, Mao YL, Yang YR, Cheng MX. First principles calculations of the single-bonded cubic phase of nitrogen. *Phys Rev B* 2006; 73: 012101.