DE GRUYTER DOI 10.1515/htmp-2012-0155 — High Temp. Mater. Proc. 2013; 32(4): 383–389

Hamit Yurtseven* and Özge Akay

Analysis of the Raman Frequency Shifts for the Lattice Modes and Vibrons Related to the Thermodynamic Quantities in the η Phase of Solid Nitrogen

Abstract: The thermodynamic quantities of the isothermal compressibility, thermal expansion and the specific heat are calculated here as a function of pressure by using the observed Raman frequencies of the lattice modes and vibrons in the η phase of solid nitrogen. The Pippard relations and their spectroscopic modifications are constructed, and the slope dP/dT is deduced from the Raman frequency shifts in this phase of N_2. It is shown that the thermodynamic quantities can be predicted from the Raman frequency shifts, in particular, in the η phase of solid nitrogen.

Keywords: Raman frequency, thermodynamic quantities, η phase, solid nitrogen

PACS® (2010). 64.10.+h, 64.60.-i, 64.70.-p

1 Introduction

The existence of the solid phase η-N_2 has been reported in the literature from a Raman experiment when the lower-frequency vibron splits at a pressure of 20 GPa at room temperature [1], as also pointed out in a previous work [2]. Close to the η phase, it has also been observed from the Raman scattering that the vibrational frequency shifts exhibit an anomalous behavior with decreasing temperature in the δ phase of nitrogen [3]. This has been interpreted as the transition due to changes in the orientational behavior of the N_2 molecules from a free rotation into an orientationally localized mode at 10.5 GPa at room temperature (300 K) [4]. An evidence has been found from the high-pressure Raman scattering for a dynamical freezing of the N_2 molecules within the δ phase and the δ-Є transition has been observed by a drop of the vibrational linewidths around 17 GPa [4]. The Raman experiments have determined that the η phase is the nonmolecular phase which occurs at around 135 GPa in the solid nitrogen [5]. The experimental P-T phase diagram of N_2 as given in a previous work [2], has been constructed using the experimental data [1], [2], [6–9]. It includes the phases of Є, δ, ζ and η, and also the low temperature–low pressure phases of α, β and γ of solid N_2. The α, β and γ phases have been studied extensively by using various experimental techniques, mainly the Raman spectroscopy [2], [4], [5], [10–12] and x-ray diffraction [1], [5], [9]. We have also studied recently the temperature dependence of the Raman frequencies of the lattice and internal modes for the γ and β phases [13]. Some theoretical studies on the α, β and γ phases have also been reported in the literature [13–17]. Thermodynamic properties of the solid nitrogen have also been studied for various phases. Studies on the thermal expansivity [18], [19] and the specific heat [20] have been given in the literature. The volume dependence of the Raman frequencies of the lattice and internal modes through the mode Grüneisen parameter has been studied extensively in the α, β and γ phases of N_2 [12].

In this study, we relate the Raman frequency shifts for the lattice (external) modes and vibrons (internal modes) of N_2 to the thermodynamic quantities such as the isothermal compressibility κ_T, thermal expansion α_p and the specific heat $C_p - C_v$ for the η phase of solid N_2. By using the experimental data [2] for the pressure dependence of the lattice modes (υ'_{L1} and υ'_{L2}) and internal modes (υ_1 and $\upsilon_{2c(2)}$), the critical behavior of the isothermal compressibility κ_T close to the η-δ transition is investigated. The pressure dependences of α_p and $C_p - C_v$ are then calculated. The spectroscopic modification of the Pippard relation, α_p vs. $(1/\upsilon)(a\upsilon/aP)_T$, for the lattice and internal modes is examined in the η phase of solid nitrogen. Also, the Pippard relation of $C_p - C_v$ vs. α_p is calculated from the frequency

---

***Corresponding author: Hamit Yurtseven:** Department of Physics, Middle East Technical University, Ankara 06531, Turkey
E-mail: hamit@metu.edu.tr
Özge Akay: Department of Physics, Middle East Technical University, Ankara 06531, Turkey; Department of Physics, Bilkent University, Ankara 06800, Turkey

Raman modes	υ_0 (cm)$^{-1}$	c′ (cm^{-1}/GPa^2)	c′	c_0	$c_1 \times 10^{-2}$ (GPa)$^{-1}$	$c_2 \times 10^{-4}$ (GPa)$^{-2}$
υ'_{L1}	276.31	5.22	_	1.1	2.36	3.0
υ'_{L2}	179.43	4.35	_	2.1	3.19	5.0
υ_1	2332.9	3.5	−0.024	0.05	0.17	1.0
$\upsilon_{2c(2)}$	2325.2	2.93	−0.027	0.01	0.33	0.5

Table 1: Values of the coefficients ν_0 and c for the pressure shifts of the N_2 lattice mode vibrons (υ'_{L1} and υ'_{L2}) (Eq. 1) and for the internal modes (υ_1 and $\upsilon_{2c(2)}$) (Eq. 2). Values of the coefficients c_0, c_1 and c_2 for the Grüneisen parameter γ_T of the Raman modes indicated according to Eq. (3), are also given here.

shifts of those Raman modes is constructed for the η phase of solid N_2.

Below, in section 2 we give our analysis and results. Discussion and conclusions are given in sections 3 and 4, respectively.

2 Calculations and results

The pressure dependences of the Raman frequency shifts for the lattice modes and vibrons were analyzed and they were related to the thermodynamic quantities of the isothermal compressibility κ_T, thermal expansion α_p and the specific heat ($C_p - C_v$) in the η phase of solid nitrogen.

2.1 Raman frequency shifts of the lattice modes and N_2 vibrons

The Raman frequencies for the lattice modes of υ'_{L1} and υ'_{L2} which were measured at various pressures (T = 300 K) [2], were analyzed for the η phase of N_2 using

$$\upsilon = \upsilon_0 + cP \tag{1}$$

where υ_0 and c are constants. For this analysis, the coefficients υ_0 and c were determined as given in Table 1. Fig. 1 gives the Raman frequencies plotted as a function of pressure (T = 300 K) for the lattice modes (υ'_{L1} and υ'_{L2}). Solid lines in this figure represent Eq. (1) fitted to the experimental data [2].

For the internal modes of υ_1 and $\upsilon_{2c(2)}$, a quadratic polynomial fit was employed to the experimental data [2] according to

$$\upsilon = \upsilon_0 + cP + c'P^2 \tag{2}$$

where υ_0, c and c′ are constants. Our fit gave us the values of the coefficients, as given in Table 1. Fig. 2 gives a plot of Raman frequency as a function of pressure for the internal modes (υ_1 and $\upsilon_{2c(2)}$) in the η phase of solid N_2.

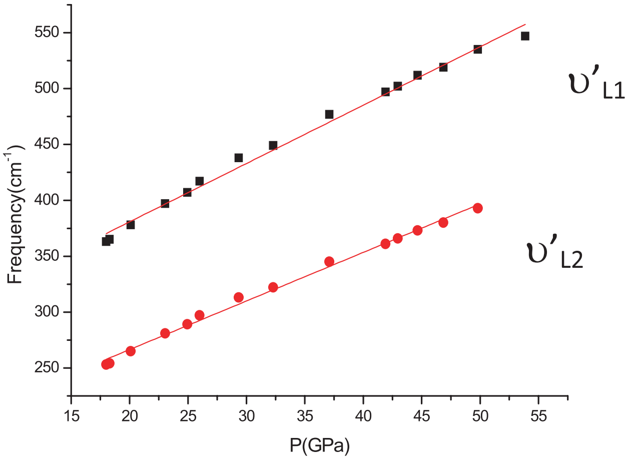

Fig. 1: The experimental Raman frequencies of the lattice modes υ'_{L1} and υ'_{L2} [2] as a function of pressure in the η phase of solid N_2. Solid lines represent Eq. (1) fitted to the experimental data with the coefficients υ_0 and c (Table 1).

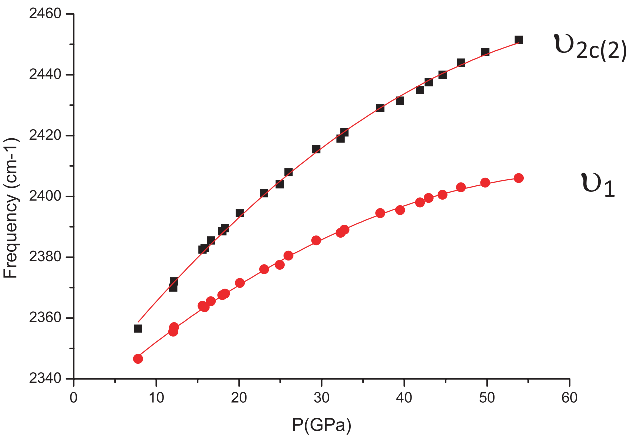

Fig. 2: The experimental Raman frequencies of the internal modes υ_1 and $\upsilon_{2c(2)}$ [2] as a function of pressure in the η phase of solid N_2. Solid lines represent Eq. (2) fitted to the experimental data with the coefficients υ_0, c and c′ (Table 1).

As the Raman frequency shifts, the mode Grüneisen parameters of the N_2 lattice modes and vibrons are also pressure dependent, which have been determined from the experimental measurements in the η phase of solid

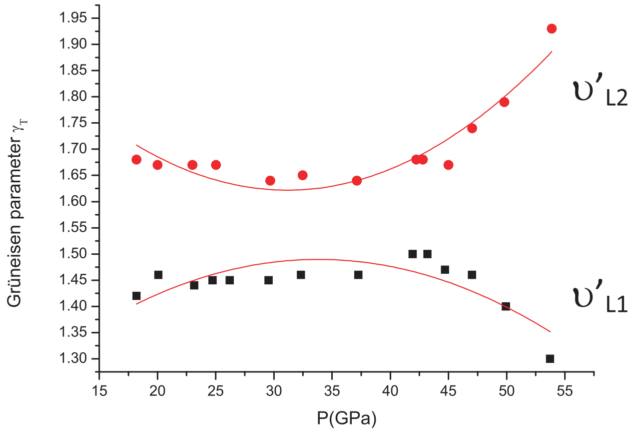

Fig. 3: Grüneisen parameter γ_T of the lattice modes of υ'_{L1} and υ'_{L2} as a function of pressure for solid N_2 [2]. Solid curves represent Eq. (3) fitted to the experimental data [2] with the coefficients c_0, c_1 and c_2 (Table 1).

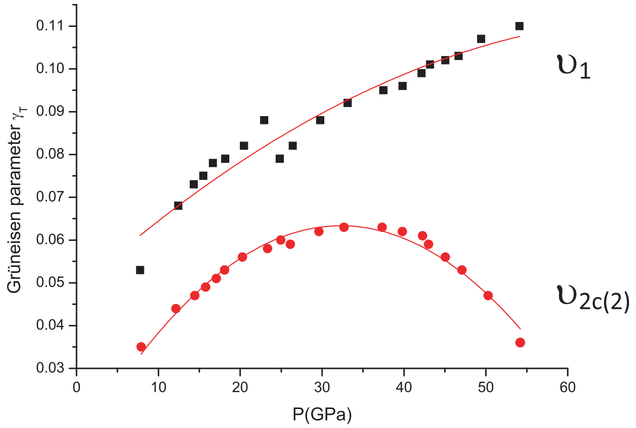

Fig. 4: Grüneisen parameter γ_T of the N_2 vibrons (υ_1 and $\upsilon_{2C(2)}$) as a function of pressure for solid N_2 [2]. Solid curves represent Eq. (3) fitted to the data [2] with the coefficients c_0, c_1 and c_2 (Table 1).

nitrogen [2]. The pressure dependence of the isothermal mode Grüneisen parameter γ_T can be expressed as

$$\gamma_T = c_0 + c_1P + c_2P^2 \tag{3}$$

where c_0, c_1 and c_2 are constants. Eq. (3) was also fitted to the experimental data [2] given for the N_2 lattice and vibrons, as plotted in Figs. 3 and 4, respectively. The coefficients c_0, c_1 and c_2 were determined for these Raman modes, which we give in Table 1.

By means of the mode Grüneisen parameter, the pressure dependence of the isothermal compressibility κ_T can be predicted according to the relation

$$\gamma_T = (1/\kappa_T)(1/\upsilon)(\partial\nu/\partial P)_T \tag{4}$$

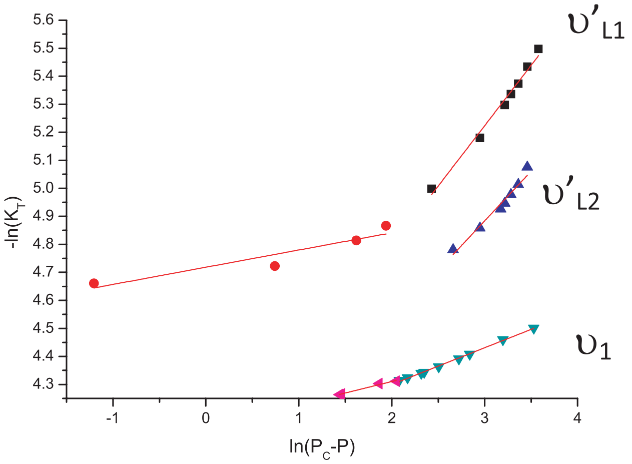

Fig. 5: The isothermal compressibility κ_T in a log-log scale as a function of pressure in the η phase close to the δ phase ($P_c = 18$ GPa) of solid N_2 at 300 K according to Eq. (5). The κ_T values were calculated using the frequency shifts of the lattice modes υ'_{L1} and υ'_{L2} and the internal mode υ_1 (Eq. 4) with the values of the critical exponent γ and the amplitude A (Table 2).

Thus, using the pressure dependence of the Raman frequency shifts for the N_2 lattice modes and vibrons with their mode Grüneisen parameters, the isothermal compressibility κ_T was predicted as a function of pressure (T = 300 K) in the η phase of solid nitrogen. This prediction of the κ_T was made close to the η-δ transition as the pressure varies (T = 300 K) around the critical pressure ($P_c = 18$ GPa) [2] according to a power-law formula,

$$K_T = A(P - P_c)^{-\gamma} \tag{5}$$

where γ is the critical exponent for the isothermal compressibility and A is the amplitude. In Fig. 5, the κ_T is plotted as a function of $P - P_c$ in a log-log scale according to Eq. (5), which was predicted using the Raman frequency shifts of the lattice modes (υ'_{L1} and υ'_{L2}) and the N_2 vibron (υ_1) (Eq. 4). The critical behavior of the isothermal compressibility κ_T was determined in the two pressure intervals (Table 2), which we plot as straight lines in Fig. 5. Table 2 gives the values of the critical exponent γ for the isothermal compressibility κ_T and the amplitude A for the pressure intervals indicated. The Raman modes whose frequency shifts were used for the critical behavior of the isothermal compressibility κ_T, are also indicated in this table. From our study, the isothermal compressibility κ_T calculated from the Raman frequency shifts of $\upsilon_{2c(2)}$ was not adequate as a function of pressure.

Raman modes	γ	A	Pressure interval $P - P_C$ (GPa)	γ	A	Pressure interval $P - P_C$ (GPa)
υ'_{L1}	0.16	0.010	$0 < P - P_C < 12$	0.43	0.020	$11 < P - P_C < 36$
υ'_{L2}	0.35	0.022	$14 < P - P_C < 32$	0.41	0.027	$19 < P - P_C < 32$
υ_1	0.06	0.015	$0 < P - P_C < 6.5$	0.13	0.018	$7 < P - P_C < 34$
$\upsilon_{2C(2)}$	0.21	7.26×10^{-6}	$0 < P - P_C < 15.5$	2.05	0.018	$42 < P - P_C < 46$

Table 2: Values of the critical exponent γ for the isothermal compressibility κ_T and the amplitude A in the pressure intervals according to Eq. (5) using the observed [2] frequency shifts of the Raman modes indicated at various pressures close to the η-δ transition in the solid N_2.

2.2 Spectroscopic modification of the Pippard relations for the η phase of N_2

Spectroscopic modifications of the Pippard relations can be obtained by relating the frequency shifts of the Raman modes studied to the thermodynamic quantities for the η phase of solid nitrogen. Using the Pippard relations [21]

$$C_P = T(dP/dT)V\alpha_P + T(dS/dT) \tag{6}$$

and

$$\alpha_P = (dP/dT)\kappa_T + (1/V)(dV/dT) \tag{7}$$

the frequency shifts ($\partial\nu/\partial P$) can be related to the thermal expansion α_p. Eq. (7) can be rewritten through the isothermal mode Grüneisen parameter γ_T (Eq. 4) as

$$\alpha_P = (1/\gamma_T)(dP/dT)\,(1/\nu)(\partial\nu/\partial P) + (1/V)(dV/dT) \tag{8}$$

Thus, a linear variation of α_p with the $(1/\nu)(\partial\nu/\partial P)_T$ can be obtained by calculating the thermal expansion α_p from the isothermal compressibility κ_T according to the thermodynamic relation

$$\alpha_P/\kappa_T = dP/dT \tag{9}$$

Since we obtained the pressure dependence of the isothermal compressibility κ_T close to the η-δ transition using Eq. (5) where the critical exponent γ and the amplitude A were determined (Table 2), the pressure dependence of the thermal expansion α_p was then determined according to Eq. (9). For this determination, the slope dP/dT was extracted from the experimental data [2]. By extending the experimental phase line between the Є and δ phases close to the phase η, to the room temperature (T = 300 K) according to a linear relation

$$P = a_0 + a_1 T \tag{10}$$

where a_0 and a_1 are constants, the slope dP/dT (= a_1) was obtained, as given in Table 3. Using this slope value and the pressure dependence of the isothermal compressibility (Eq. 5) which was obtained from the frequency shifts of the Raman modes, as given in Fig. 5, values of the thermal expansion α_p were calculated (Eq. 9) as a function of pressure (T = 300 K) close to the η phase of solid nitrogen. Figs. 6 and 7 give our plots of α_p as a function of $(1/\gamma_T)(1/\upsilon)(\partial\nu/\partial P)_T$ for the lattice modes (υ'_{L1} and υ'_{L2}) and for the internal modes (υ_1 and $\upsilon_{2c(2)}$), respectively, according to the spectroscopic modification of the Pippard relation (Eq. 8). The values of the slope dP/dT and the intercept (1/V)(dV/dT) which we extracted from the Raman modes studied, are given in Table 4.

Phases	$-a_0$ (GPa)	a_1 (GPa/K)	dP/dT (GPa/K)
η-δ	2.21	0.065	0.065

Table 3: Values of the coefficients a_0 and a_1 according to Eq. (10) which was fitted to the experimental η-δ phase line [2] in the solid N_2.

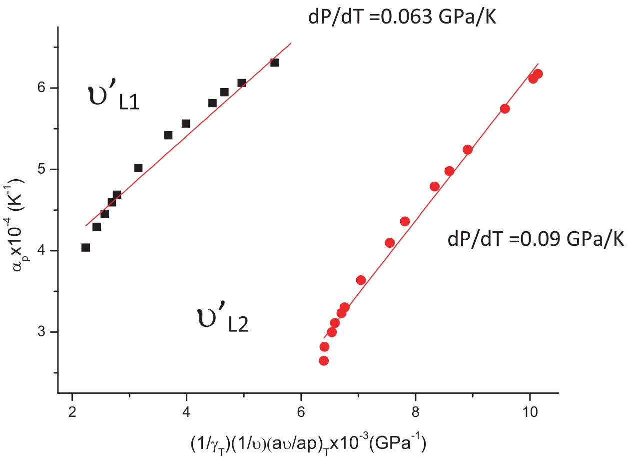

Fig. 6: Thermal expansion α_P as a function of the frequency shifts of the lattice modes (υ'_{L1} and υ'_{L2}) according to Eq. (8) for the η phase of solid N_2.

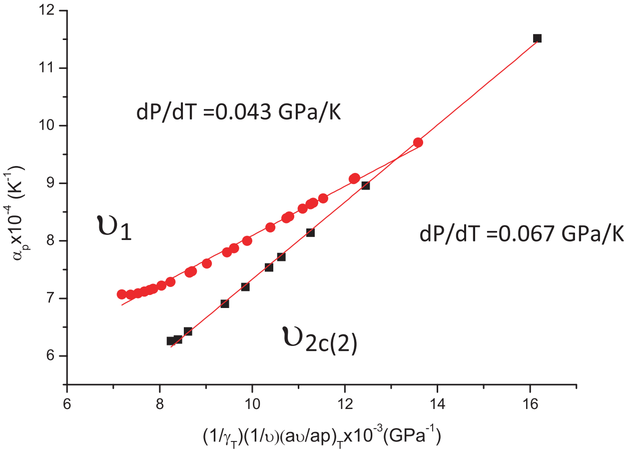

Fig. 7: Thermal expansion α_P as a function of the frequency shifts of the internal modes (υ_1 and $\upsilon_{2c(2)}$) according to Eq. (8) for the η phase of solid N_2.

Raman modes	dP/dT (GPa/K)	(1/V)(dV/dT) (K^{-1})	dP/dT (GPa/K)
υ'_{L1}	0.063	3.0	0.065
υ'_{L2}	0.096	4.0	0.065
υ_1	0.043	4.0	0.065
$\upsilon_{2c(2)}$	0.067	0.7	0.065

Table 4: Values of the slope dP/dT and the intercept (1/V)(dV/dT) according to Eqs. (7) and (8) for the Raman modes indicated in the η phase of solid N_2. dP/dT values η extracted from Eq. (11) through Eq. (8) for the Raman modes are also given.

The pressure dependence of the specific heat was also calculated in this study according to the thermodynamic relation

$$C_P - C_v = TV\,\alpha_p^2/\kappa_T \tag{11}$$

for the η phase of solid nitrogen. Using the pressure dependence of α_P and κ_T at T = 300 K, $(C_P - C_v)/V$ was obtained at various pressures in the η phase of solid nitrogen. Since the values of α_P and κ_T were obtained using the frequency shifts of the Raman modes (υ'_{L1} and υ'_{L2}, υ_1 and $\upsilon_{2c(2)}$), they were used to calculate $(C_P - C_v)/V$ as a function of pressure (T = 300 K). $(C_P - C_v)/V$ values are plotted as a function of α_P using the frequency shifts of the lattice modes (υ'_{L1} and υ'_{L2}) and the internal modes (υ_1 and $\upsilon_{2c(2)}$), respectively, in Figs. 8 and 9 according to the Pippard relation (Eq. 6) where $C_v = T(dS/dT)$. The experimental value of the slope, dP/dT = 0.065 GPa/K (Table 3) was obtained from both plots (Table 4) which was used initially as also shown in Figs. 8 and 9.

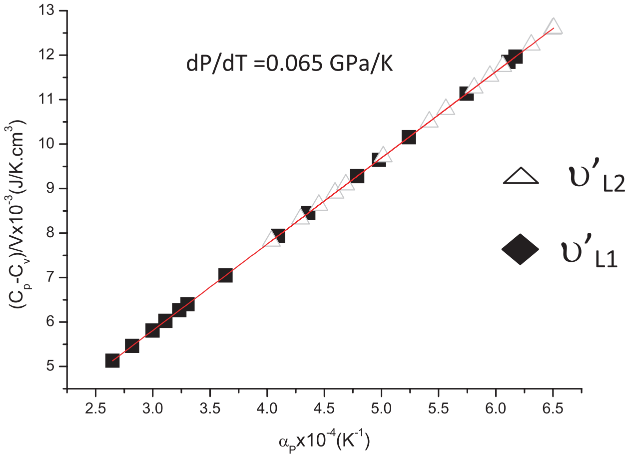

Fig. 8: The difference in the specific heat per unit volume as a function of the thermal expansion α_P according to Eq. (6) using the Raman frequencies of the υ'_{L1} and υ'_{L2} modes of solid N_2.

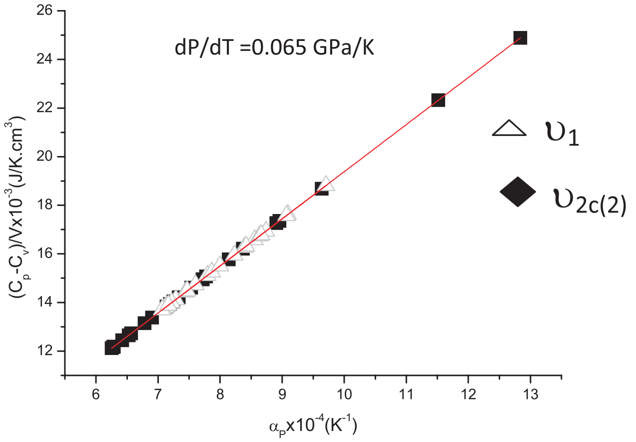

Fig. 9: The difference in the specific heat per unit volume as a function of the thermal expansion α_P according to Eq. (6) using the Raman frequencies of the υ_1 and $\upsilon_{2c(2)}$ modes for the η phase of solid N_2.

3 Discussion

The Raman frequency shifts of the N_2 lattice modes (υ'_{L1} and υ'_{L2}) and vibrons (υ_1 and $\upsilon_{2c(2)}$) were related to the thermodynamic functions of the isothermal compressibility κ_T, thermal expansion α_P and the specific heat $(C_P - C_v)$ for the η phase of solid nitrogen. These correlations were obtained by analyzing the Raman frequencies considered according to Eqs. (1) and (2), as given in Figs. 1 and 2, respectively (Table 1). The pressure dependence of the Raman frequencies was represented by linear (Eq. 1) and quadratic (Eq. 2) relations using the experimental data, as shown in the figures. The Raman frequencies of the modes studied increase as the pressure increases as obtained experimentally (Figs. 1 and 2). However, the pressure dependence of the mode Grüneisen parameters for the Raman modes except the υ_1 mode (Fig. 4) is completely different, as shown in Figs. 3 and 4. The γ_T values increase as the pressure increases up to 55 GPa for the υ_1 mode, whereas for the $\upsilon_{2c(2)}$ mode the γ_T increases with the pressure to about 30 GPa, then it decreases with increasing pressure (Fig. 4). Regarding the υ'_{L1} and υ'_{L2} modes (Fig. 3), the pressure dependence of the mode Grüneisen parameter γ_T is not very well represented by a quadratic function (Eq. 3) because of the scattered experimental data [2] for both lattice modes (Fig. 3), although the quadratic function is the best suited to the data available.

In this study, we also analyzed the critical behavior of the isothermal compressibility κ_T which was calculated using the Raman frequency shifts of the Raman modes through the mode Grüneisen parameter γ_T (Eq. 4). From the pressure dependence of the frequency shifts of both N_2 lattice modes and vibrons, values of the critical exponent γ for the κ_T were extracted (Table 2) which increase as the pressure interval increases with respect to the critical pressure P_c. For the lattice modes of υ'_{L1} and υ'_{L2} and the internal mode υ_1, this increase in the γ value is reasonable, but the value of $\gamma = 2.05$ due to the $\upsilon_{2c(2)}$ mode close to the P_c (Table 2) is too large to describe the critical behavior of κ_T in the η phase of solid nitrogen.

We finally constructed the Pippard relations here according to Eqs. (6) and (8) using the pressure dependence of the Raman modes studied for the η phase of solid N_2. As shown in Figs. 6–9, a linear variation of α_p with the $(1/\upsilon)(\partial\upsilon/\partial P)_T$ and also a linear variation of $(C_P - C_V)/V$ with the α_P were obtained. The slope value of $dP/dT = 0.065$ GPa/K was deduced from our linear plots (Figs. 8 and 9), which is the same value obtained experimentally (Table 3). In the case of α_P plotted as a function of $(1/\upsilon)(\partial\upsilon/\partial P)_T$ for the lattice modes of υ'_{L1} and υ'_{L2} (Fig. 6), values of the slope dP/dT were deviated from the experimental value of 0.065 GPa/K. Since we calculated the pressure dependence of the specific heat $(C_P - C_V)$ from Eq. (11) where the slope value of $dP/dT = 0.065$ GPa/K was used initially as the experimental value (Table 3), the same slope value should be extracted from a plot of $(C_P - C_V)/V$ vs. α_P using the Raman frequency shifts of both N_2 lattice modes (Fig. 8). On the other hand, the slope value of dP/dT deduced from the Raman frequency shifts $(1/\upsilon)(\partial\upsilon/\partial P)_T$ for the lattice modes of υ'_{L1} and υ'_{L2}, as plotted in Fig. 6, is determined by the pressure dependence of the Raman frequencies (Fig. 1) and also of the mode Grüneisen parameter γ_T (Fig. 3). In the pressure interval studied, variation of the Raman frequencies of the υ'_{L1} and υ'_{L2} modes (Fig. 1) with the pressure is well represented by Eq. (1). However, the mode Grüneisen parameter γ_T is not well represented by a quadratic function due to the scattered experimental data, as stated above. This may cause a nonlinear behavior of our plots of α_P vs. $(1/\upsilon)(\partial\upsilon/\partial P)_T$ for the lattice modes of υ'_{L1} and υ'_{L2} (Fig. 6) in the η phase of solid nitrogen according to Eq. (8). So, the slope dP/dT changes for this nonlinear behavior (Fig. 6) if we choose, say, two different pressure intervals in the η phase of solid N_2. As plotted in Fig. 7, the spectroscopic modification of the Pippard relation (Eq. 8) was obtained from a linear variation of the α_p with the frequency shifts $(1/\upsilon)(\partial\upsilon/\partial P)_T$ for both the internal modes of υ_1 and $\upsilon_{2c(2)}$. This linear variation deviates as the frequency shifts decrease for the υ_1 mode (Fig. 7), whereas for the $\upsilon_{2c(2)}$ mode this linearity is better represented by Eq. (8). This linear variation of α_p with the $(1/\upsilon)(\partial\nu/\partial P)_T$ for the $\upsilon_{2c(2)}$ mode (Fig. 7) gives rise to the experimentally obtained value between the phases η and δ in solid N_2 (Tables 3 and 4). On the other hand, the dP/dT value extracted from the Raman frequency shifts of the $\nu_{2c(2)}$ mode is not too far away from the experimental value of 0.065 GPa/K (Table 4). When we plotted $(C_P - C_v)/V$ vs. α_p using the Raman frequency shifts of the υ_1 and $\upsilon_{2c(2)}$ modes, as given in Fig. 9, linear variations were obtained according to Eq. (6), from which the slope value of $dP/dT = 0.065$ GPa/K (Table 4) was extracted, as for the lattice modes of υ'_{L1} and υ'_{L2}. This slope value is the same as the experimental dP/dT value (Table 3). A linear variation of $(C_P - C_v)/V$ vs. α_p (Figs. 8 and 9) and the dP/dT values deduced, also validates the Pippard relation (Eq. 6) through the spectroscopic modification of the Pippard relation (Eq. 8) for the N_2 lattice modes and vibrons in the η phase of solid nitrogen.

Finally, regarding the quadratic pressure dependence of the isothermal mode Grüneisen parameter (Eq. 3) we deduced the γ_T values of the lattice modes at zero pressure $(P = 0)$ with the coefficient c_0 (Table 1) as 1.1 (υ'_{L1}) and 2.1 (υ'_{L2}). Our value of $\gamma_T = 1.1$ for the υ'_{L1} is close to the value of 5/6 expected for a quadrupolar interaction potential using the quasi-harmonic approximation and it is also in the range of $1 < \gamma \leq 1.5$ due to nuclear quadrupole resonance methods [22]. Our γ_T values for the internal modes (υ_1 and $\upsilon_{2c(2)}$) are too small to be compared with the model expectations.

4 Conclusions

The experimental Raman frequency shifts and the mode Grüneisen parameters were analyzed for the N_2 vibrons at various high pressures (T = 300 K) in the η phase of solid nitrogen. The critical behavior of the isothermal compressibility calculated from the Raman frequency shifts was described by the critical exponent close to the η-δ transition. By calculating the pressure dependence of the thermal expansion and the specific heat, the Pippard relations (and their spectroscopic modification) were established in the η phase of solid nitrogen.

Our results show that the thermodynamic quantities can be calculated from the Raman frequency shifts and that the Pippard relations can be verified for the η phase of solid nitrogen.

Received: October 19, 2012. Accepted: November 30, 2012.

References

[1] R. Reichlih, D. Schferl, S. Martin, C. Vanderborgh and R.L. Mills, Phys. Rev. Lett. 55 (1985) 1464.

[2] H. Schneider, W. Hafner, A. Wokaun and H. Olijnyk, J. Chem. Phys. 96 (1992) 8046.

[3] M.M. Scheerboom and J.A. Schouten, Phys. Rev. Lett. 71 (1993) 2252.

[4] T. Westerhoff, A. Wittig and R. Feile, Phys. Rev. B54 (1996) 14.

[5] E. Gregoryanz, A.F. Goncharov, R.J. Hemley, H.K. Mao, M. Somayazulu and G. Shen, Phys. Rev. B66 (2002) 224108.

[6] M. Grimsditch, Phys. Rev. B32 (1985) 514.

[7] R.L. Mills, B. Olinger and D.T. Cromer, J. Chem. Phys. 84 (1986) 2837.

[8] D. Schiferl, R. Lesar and D.S. Moore, in The Simple Molecular Systems at Very High Density (Les Houches, France, 1988), edited by A. Polian, P. Loubeyre and N. Boccara (Plenum, New York, 1989), p. 303.

[9] H. Olijnyk, J. Chem. Phys. 93 (1990) 8968.

[10] A. Anderson, T.S. Sun and M.C.A. Donkersloot, Can. J. Phys. 48 (1970) 2265.

[11] M.M. Thiery, D. Fabre, M. Jean-Louis and H. Vu, J. Chem. Phys. 59 (1973) 4559.

[12] F.D. Medina and W.B. Daniels, J. Chem. Phys. 64 (1976) 150.

[13] H. Yurtseven and T. Tunay, Int. J. Mod. Phys. 24 (2010) 6069.

[14] T.S. Kuan, A. Warshel and O. Schnepp, J. Chem. Phys. 52 (1970) 3012.

[15] T. Luty and G.S. Pawley, Chem. Phys. Lett. 28 (1974) 593.

[16] M.J. Mandell, J. Low Temp. Phys. 17 (1974) 169.

[17] A. Zunger and E. Huler, J. Chem. Phys. 62 (1975) 3010.

[18] V.G. Manzhelii, A.M. Tolkachev and E.I. Vortovich, Phys. Stat. Sol. 13 (1966) 351.

[19] D.C. Heberlein, E.D. Adams and T.A. Scott, J. Low Temp. Phys. 2 (1970) 449.

[20] M.I. Bagatskii, V.A. Kutcheryavy, M.G. Manzhalii and V.A. Popov, Phys. Stat. Sol. 26 (1968) 453.

[21] A.B. Pippard, *The Flements of Classical Thermodynamics,* Cambridge Univ. Press, New York, 1957.

[22] J.R. Brookeman, M.M. McFnan and T.A. Scott, Phys. Rev. B4 (1971) 3661.