THERMODYNAMIC PROPERTIES OF MOLECULAR CRYOCRYSTALS OF NITROGEN TYPE WITH FCC STRUCTURE: CONTRIBUTION FROM LATTICE VIBRATIONS AND MOLECULAR ROTATIONAL MOTION

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Abstract. *The analytic expressions of thermodynamic quantities such as the Helmholtz free energy, the internal energy, the entropy, the molar specific heats under constant volume and under constant pressure, etc. of molecular cryocrystals of N_2 type with fcc structure are obtained by the statistical moment method and the self-consistent field method taking account of the anharmonicity in lattice vibrations and molecular rotational motion. Numerical results for molecular cryocrystals of N_2 type ($\alpha - N_2$, $\alpha - CO$) are compared with the experimental data.*

I. INTRODUCTION

Molecular crystals, comprising a vast and comparatively scarcely investigated class of solids, are characterized by a diversity of properties. Up to now only solidified noble gases have systematically been investigated and this is due to the availability of the relevant theoretical models and to the ease of comparing theories with experimental results. Recently experimental data have been obtained for simple non-monoatomic molecular crystals as well, which in turn has stimulated the appearance of several theoretical papers on that subject. This paper deals with the analysis of thermodynamic properties of the group of non-monoatomic molecular crystals including solid N_2 and CO that have similar physical properties. These crystals are formed by linear molecules and in their ordered phase, the molecular centres of mass are situated at the site of fcc pattern, the molecular axes being directed the four spatial diagonals of a cube (space group $Pa3$). The characteristic feature of the intermolecular interaction in such crystals is that the non-central part of the potential results from quadrupole forces and from the part of valency and dispersion forces having the analogous angular dependence as quadrupole forces, and further, that dipole interaction either does not exist (N_2) or is negligible (CO) to influence the majority of thermodynamic properties. In addition, all crystals considered have a common feature, namely their intrinsic rotational temperatures $B = \hbar^2/2I$ (I is the momentum of inertia

of the corresponding molecule) are small compared to the energy of non-central interaction. In the low-temperature range, it is reasonable to apply an assumption successfully used by the authors [1, 2] that translational motions of the molecular system are independent. As shown [3] there are two types of excitations in molecular crystals phonons and librons and furthermore, the thermodynamic functions can be written as a sum of two independent terms corresponding to each subsystem. In such a treatment, the translational orientational interaction leads to a renormalization of the sound velocity and of the libron dispersion law only. The investigation of the librational behavior of molecules is usually carried out within the framework of the harmonic approximation. However, anharmonic effects for the thermodynamic properties are essential at temperatures substantially lower than the orientational disordering temperature. The effect of molecular rations in N_2 and CO crystals not restricted by the assumption of harmonicity of oscillations has been calculated numerically in the molecular field approximation by Kohin [4]. Full calculations on thermodynamic properties of molecular crystals of type N_2 are given by the statistical moment method (SMM) in [5, 6] and by self-consistent field method (SCFM) in [9]. In [7], the low temperature heat capacity at constant volume of the molecular crystals of type N_2 is studied by combining the SMM and the SCFM. This paper represents further investigations of anharmonic effects of lattice vibrations and molecular rotations on other thermodynamic properties (such as the free energy, the energy, the entropy, the heat capacity at constant pressure, etc) of the crystals of type N_2.

II. THEORY

Using SMM, only taking account of lattice vibration, the vibrational free energy of crystals with fcc structure is approximately determined by the following expression [8]:

$$\Psi_{vib} \approx V_0 + \Psi_{0vib} + 3N\{\frac{\theta^2}{k^2}[\gamma_2 X^2 - \frac{2\gamma_1}{3}(1 + \frac{X}{2})]\frac{2\theta^3}{k^4}[\frac{4}{3}\gamma_2^2 X(1 + \frac{X}{2}) -$$

$$-2(\gamma_1^2 + 2\gamma_1\gamma_2)(1 + \frac{X}{2})(1 + \frac{X}{2})]\} ,$$

$$\Psi_{0vib} = 3N\theta[x + ln(1 - e^{-2x})], x = xcothx, k = \frac{1}{2}\sum_i(\frac{\partial^2\varphi_{i0}}{\partial u_{i\alpha}^2})_{eq},$$

$$\gamma_1 = \frac{1}{48}\sum_i(\frac{\partial^4\varphi_{i0}}{\partial u_{i\alpha}^2\partial u_{i\beta}^2})_{eq} ,$$

$$where \quad \alpha \neq \beta; \alpha, \beta = x, y, z; \theta = k_B T; k = m\omega^2; x = \hbar\omega/2\theta; U_0 = (N/2)\sum_i \varphi_{i0} . (1)$$

where k_B is the Boltzmann constant, T is the absolute temperature, m is the mass of particle at lattice node, ω is the frequency of lattice vibration,k, γ_1 and γ_2 are the parameters of crystal depending on the structure of crystal lattice and the interaction potential between particles at nodes, φ_{i0} is the interaction potential between the ith particle, and the 0th particle, $u_{i\alpha}$ is the displacement of ith particle from equilibrium position in the direction α and N is the number of particles per mole or the Avogadro number. This formula permits to find the free energy at temperature T if knowing the value of parameters

k, γ_1 and γ_2 at temperature T_0 (for example $T_0 = 0$ K). If T_0 is not far from T, then we can see that the vibration of a particle around a new equilibrium position (corresponding to T_0) is harmonic. Therefore, the vibrational free energy of crystal is that of N harmonic oscillators:

$$\Psi_{vib} \approx 3N \left\{ \frac{u_0}{6} + \theta \left[x + ln(1 - e^{-2x}) , \right] \right\}; u_0 = \sum_i \varphi_{i0} . \tag{2}$$

Using SCFM, only taking account of molecular rotation, the rotational free energy of crystals with fcc structure in pseudo-harmonic approximation (when $U_0\eta/B \geq 1$ or $T/\sqrt{(U_0 B\eta)} \leq 1$) is determined by [9]:

$$\frac{\Psi_{rot}}{k_B N} = 2Tln \left[4sinh(\frac{\varepsilon}{2T}) \right] - U_0\eta + \frac{U_0\eta^2}{2}; \varepsilon = \sqrt{6a_0 B\eta} . \tag{3}$$

where U_0 is the barrier, which prevents the molecular rotation at $T = 0$ K, $B = \hbar^2/2I$ is the intrinsic rotational temperature or the rotational quantum or the rotational constant and η is the ordered parameter In classical approximation (when $T/\sqrt{U_0 B\eta} \gg 1$, the rotational free energy has the form [9]:

$$\frac{\Psi_{rot} - \Psi_{0rot}}{Nk_B} = \frac{U_0\eta}{2} + \frac{U_0\eta^2}{2} + T \int_0^1 d(\cos\vartheta) exp \left(\frac{3}{2} \frac{U_0\eta}{T} \cos^2\vartheta \right) . \tag{4}$$

where Ψ_{rot} is the rotational free energy of the system of non-interaction rotators and is one of angles determining the position of symmetric axe of molecular field for the coordinate system of crystal. In self-consistent libron approximation (SCLM), the rotational free energy of crystal becomes [9]:

$$\frac{\Psi_{rot}}{k_B N} = 2Tln \left[4sinh\frac{\eta}{2T} \right] - \frac{\eta}{2}coth \left(\frac{\eta}{2T} \right) - \frac{B}{2} - \frac{U_0\eta^2}{2} , \tag{5}$$

Taking account of both lattice vibration and molecular rotation, the total free energy of crystal is the sum of the vibrational free energy and the rotational free energy:

$$\Psi = \Psi_{vib} + \Psi_{rot} . \tag{6}$$

The energy of crystal lattice in pseudo-harmonic approximation has the form:

$$E = \Psi - T\left(\frac{\partial\Psi}{\partial T}\right)_V = E_{vip} + E_{rot} \ ,$$

where :

$$E_{vib} = \Psi_{vib} - T\left(\frac{\partial\Psi_{vib}}{\partial T}\right)_V$$

$$= U_0 + E_{0vib} + \frac{3N\theta^2}{k^2}\left[\gamma_2 X^2 + \frac{\gamma_1}{3}(2+Y^2) - 2\gamma_2 XY^2\right]$$

$$E_{0vib} = 3N\theta X$$

$$E_{rot} = \Psi_{rot} - T\left(\frac{\partial\Psi_{rot}}{\partial T}\right)_V = -Nk_B U_0\left[1 + \frac{3B}{\varepsilon}coth\left(\frac{\varepsilon}{2T}\right)\right] + \frac{Nk_B U_0}{2}\left[1 - \frac{3B}{\varepsilon}coth\left(\frac{\varepsilon}{2T}\right)\right]^2 -$$

$$- Nk_B\left(T\frac{\partial\varepsilon}{\partial T} - \varepsilon\right)coth\left(\frac{\varepsilon}{2T}\right) +$$

$$+ \frac{3Nk_B U_0 BT}{2\varepsilon^2}\left[1 + \frac{3B}{\varepsilon}coth\left(\frac{\varepsilon}{2T}\right)\right]\left\{\frac{\varepsilon}{2T^2}\left(T\frac{\partial\varepsilon}{\partial T} - \varepsilon\right)\left[1 - coth^2\left(\frac{\varepsilon}{2T}\right)\right] - \frac{\partial\varepsilon}{\partial T}\left(\frac{\varepsilon}{2T}\right)\right\}(7)$$

The entropy of crystal lattice in pseudo-harmonic approximation has the form:

$$S = \frac{E - \Psi}{T} = S_{vib} + S_{rot}$$

$$S_{vib} = -k_B\left(\frac{\partial\Psi}{\partial\theta}\right)_V = S_{ovib} + \frac{3Nk_B\theta}{k^2}\left[\frac{\gamma_1}{3}(4 + X + Y^2) - 2\gamma_2 XY^2\right],$$

where :

$$X = xcothx; Y = \frac{x}{sinhx}; S_{ovib} = 3Nk_B[xcothx - ln(2sinhx)]$$

and :

$$S_{rot} = \frac{E_{rot} - \Psi_{rot}}{T} = -2Nk_B ln[4sinh(\frac{\varepsilon}{2T})] - \frac{Nk_B}{T}(T\frac{\partial\varepsilon}{\partial T} - \varepsilon)coth(\frac{\varepsilon}{2T}) +$$

$$+ \frac{3Nk_B U_0 BT}{2\varepsilon^2}[1 + \frac{3B}{\varepsilon}coth(\frac{\varepsilon}{2T})]\{\frac{\varepsilon}{2T^2}(T\frac{\partial\varepsilon}{\partial T} - \varepsilon)[1 - coth^2(\frac{\varepsilon}{2T})] -$$

$$- \frac{\partial\varepsilon}{\partial T}(\frac{\varepsilon}{2T})\} \ . \tag{8}$$

The isothermal compressibility and the thermal expansion coefficient are only determined by SMM as in [8]. The molar heat capacity at constant volume in pseudo-harmonic approximation is determined by the following expressions [7]:

$$C_V = C_V^{rot} + C_V^{vib} = -T\left(\frac{\partial^2\Psi}{\partial T^2}\right)_V - T\left(\frac{\partial^2\Psi_{rot}}{\partial T^2}\right)_V$$

$$C_V^{vib} = 3Nk_B\left\{Y^2 + \frac{2\theta}{k^2}\left[\left(2\gamma_2 + \frac{\gamma_1}{3}\right)XY^2 + \frac{2\gamma_1}{3} - \gamma_2(Y^4 + 2X^2Y^2)\right]\right\}$$

$$C_V^{rot} = \frac{Nk_B}{2}\frac{(\varepsilon/T)^2}{sinh^2(\varepsilon/2T)}\left(1 - \frac{T}{\varepsilon}\frac{\partial\varepsilon}{\partial T}\right) \ , \tag{9}$$

The molar heat capacity at constant volume in pseudo-harmonic approximation is determined by the following expression [8]:

$$C_P = C_V + \frac{9TV\alpha^2}{\chi_T}, V = N_V = N\frac{\sqrt{2}}{2}a^3 \ . \tag{10}$$

III. NUMERICAL RESULTS AND DISCUSSION

In order to apply the theoretical results in Section 2 to molecular cryocrystals of nitrogen type, we use the Lennard-Jones (LJ) potential:

$$\varphi(r) = 4\varepsilon_1 \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] , \tag{11}$$

where $\varepsilon_1/k_B = 95.05K; \sigma = 3.698 \times 10^{-10}m$ for $\alpha - N_2$; $\varepsilon_1/k_B = 110K; \sigma = 3.59 \times 10^{-10}m$ for $\alpha - CO$ [5]. In the approximation of two first coordination spheres, the crystal parameters are given by:

$$
\begin{aligned}
k &= \frac{4\varepsilon_1}{a^2} \left(\frac{\sigma}{a}\right)^6 \left[265.298 \left(\frac{\sigma}{a}\right)^6 - 64.01 \right] \\
\gamma_1 &= \frac{4\varepsilon_1}{a^4} \left(\frac{\sigma}{a}\right)^6 [803.555 \left(\frac{\sigma}{a}\right)^6 - 40.547] \\
\gamma_2 &= \frac{4\varepsilon_1}{a^4} \left(\frac{\sigma}{a}\right)^6 \left[3607.242 \left(\frac{\sigma}{a}\right)^6 - 305.625 \right] .
\end{aligned}
\tag{12}
$$

where α is the nearest neighbour distance at temperature T. The LJ potential has a minimum value corresponding to the position $r_0 = \sigma \sqrt[6]{2} \approx 1.2225\sigma$ However, since there is interaction of many particles, the nearest neighbour distance α_0 in the lattice is smaller than r_0. It is equal to $\alpha_0 = r_0 \sqrt[6]{A_{12}/A_6} \approx 1.0902\sigma$ where A_6 and A_{12} are the structural sums and they have the values $A_6 = 14.454; A_{12} = 12.132$ for a fcc crystal [8]. From the above mentioned results, we obtain the values of crystal parameters at 0 K. From that, we calculate the nearest neighbour distances of the lattice, the vibrational free energy and other thermodynamic quantities (the entropy, the energy, the isothermal compressibility, the thermal expansion coefficient, the molar heat capacities at constant volume and at constant pressure,etc. in different temperatures by SMM as in [5]. The values of B, U_0 and the values of η at various temperatures are given in Tables 1- 3 [9].

Table 1. Values of B and U_0 for crystals of N_2 type

Crystal	$\alpha - N_2$	$\alpha - CO$
$B(K)$	2.8751	2.7787
$U_0(K)$	325.6	688.2

Table 2. Values of η at various temperatures for $\alpha - N_2$

$T(K)$	0	10	15	20	24	28	30	32	34
η	0.8633	0.8617	0.8544	0.8404	0.8244	0.8038	0.7916	0.7778	0.7621

Table 3. Values of η at various temperatures for $\alpha - CO$

$T(K)$	0	10	20	30	36	42	52	56	60
η	0.9100	0.9099	0.9060	0.8942	0.8832	0.8690	0.8364	0.8188	0.7973

The temperature dependences of the thermodynamic quantities (the free energy, the entropy, the energy, the molar heat capacity at constant volume, the molar heat capacity at constant pressure) for molecular cryocrystals of nitrogen type calculated by SMM and SCFM are represented in Figures.1-5. In comparison with experiments, the heat capacity calculated by both SMM and SCFM is better than the

heat capacity calculated by only SMM or only SCFM. Both the lattice vibration and the molecular rotation have important contributions to thermodynamic properties of molecular cryocrystals of nitrogen type.
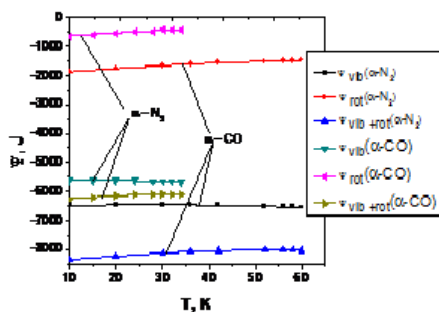

Fig. 1. Vibrational free energy, rotational free energy and total free energy at various temperatures for crystals of N_2 type
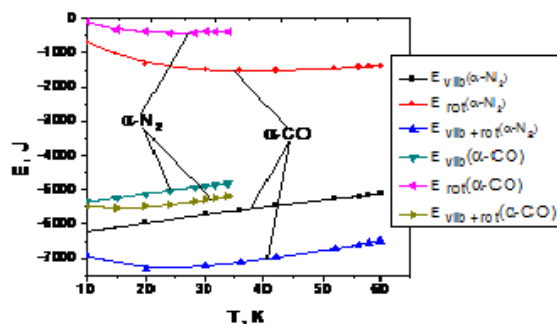

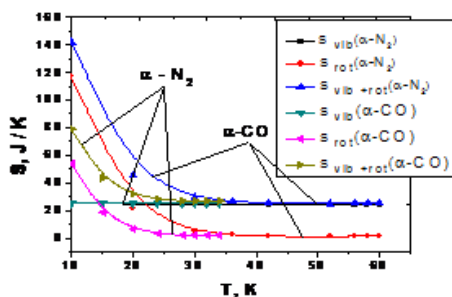**Fig. 2.** Vibrational energy, rotational energy and total energy at various temperatures for crystals of N_2 type

Fig. 3. Vibrational entropy, rotational entropy and total entropy at various temperatures for crystals of N_2 type
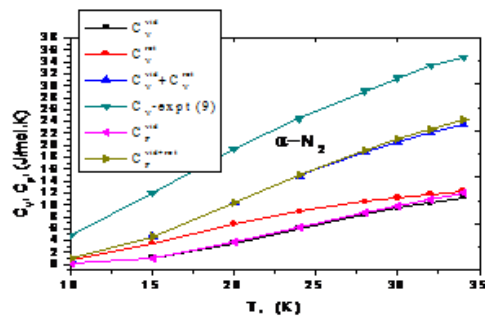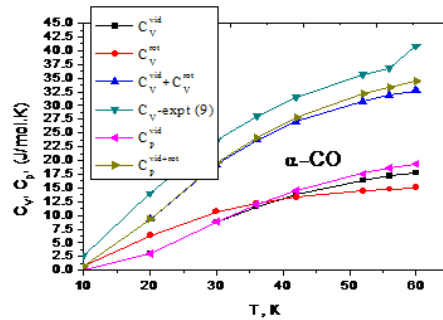

Fig. 4. Heat capacities at constant volume and at constant pressure in different temperatures for N_2 crystal

Fig. 5. Heat capacities at constant volume and at constant pressure in different temperatures for CO crystal

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