

SPECIFIC HEAT AT CONSTANT VOLUME FOR CRYOCRISTALS OF NITROGEN TYPE

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Abstract. *Specific heats at constant volume of molecular cryocrystals of N_2 type are studied by combining the statistical moment method and the self-consistent field method taking account of lattice vibrations and molecular rotational motion. Theoretical results are applied to molecular cryocrystals of N_2 type such as N_2 , CO , N_2O and CO_2 cryocrystals and numerical results are compared with the experimental data.*

I. INTRODUCTION

The study of specific heat for cryocrystals of nitrogen type is interested experimentally by many researchers. For example, specific heat of solid nitrogen in the interval of 16-61K is determined firstly by Eucken [1]. Specific heat of nitrogen in low temperatures is measured by Bagatskii, Kucheryavy, Manzhelii and Popov [2] (2.6-14.5K), Burford and Graham [3](0.8-4.2K) and Sumarokov, Freiman, Manzhelii and Popov [4](1.8-8K). Theoretically, specific heat of solid nitrogen and monoxide carbon is investigated by the theory accounting anharmonic and correlational effects, the self-consistent field theory, the quasianharmonic theory [5] and the statistical moment theory (SMM) [6,7]. Analogous research results for α -CO, CO_2 and N_2O cryocrystals also are summarized fully in [5]. In our previous papers [6, 7], the specific heat at constant volume of cryocrystals of nitrogen type is calculated by the statistical moment method taking account of only lattice vibrations and not molecular rotations. Our calculated results only agreed qualitatively with experiments. Idea of applying the self-consistent field method (SCFM) in order to describe phenomena relating to orientation transition is firstly proposed by Frenkel [8] and Fowler [9]. First quantitative calculations of crystals N_2 , CO based on the SCFM are carried out by Kohin [10], where he calculated the energy of basic state and the energy of librational excitations at zero temperature. More full calculations of thermodynamic properties for crystals of nitrogen type are performed in [11-13]. In the present study, specific heats at constant volume of molecular cryocrystals of N_2 type are studied by combining the statistical moment method and the self-consistent field method taking account of lattice vibrations and molecular rotational motion. Theoretical results are applied to molecular cryocrystals of N_2 type such as N_2 , CO, N_2O and CO_2 cryocrystals and numerical results are compared with the experimental data. The format of the present paper is as follows: In Sec.II, we present the statistical moment method in deriving the specific heat at constant volume of crystals with fcc structure taking account of lattice vibration and

the self-consistent field method in the study of specific heat at constant volume of crystals of nitrogen type taking account of molecular rotation. Our calculated vibrational and rotational specific heats for molecular cryocrystals of N_2 type such as N_2 , CO, N_2O and CO_2 cryocrystals are summarized and discussed in Sec.III.

II. THEORY OF SPECIFIC HEAT AT CONSTANT VOLUME FOR MOLECULAR CRYOCRYSTAL OF NITROGEN TYPE

II.1. Theory of vibrational specific heat at constant volume for crystal with cubic structure

Using SMM, only taking account of lattice vibration, the specific heat at constant volume of crystals with the fcc structure is determined by the following expression [14]

$$C_v = 3Nk_B \left\{ \frac{x^2}{sh^2x} + \frac{2\theta}{k^2} \left[\left(2\gamma_2 + \frac{\gamma_1}{3} \right) \frac{x^3cth x}{sh^2x} + \frac{2\gamma_1}{3} - \gamma_2 \left(\frac{x^4}{sh^2x} + \frac{2x^4cth^2x}{sh^2x} \right) \right] \right\}; \quad (1)$$

$$x = \frac{\omega}{2\theta}, \quad k = \frac{1}{2} \sum_i \left(\frac{\partial^2_{i\varphi_0}}{\partial u_{i\varphi_0}^2} \right) \equiv m\omega^2$$

$$\gamma = \frac{1}{12} \sum_i \left[\left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\beta}^4} \right)_{eq} + 6 \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\beta}^2 \partial u_{i\gamma}^2} \right)_{eq} \right], \quad (2)$$

$$\gamma_1 = \frac{1}{48} \sum_i \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\beta}^4} \right)_{eq}, \quad \gamma_2 = \frac{1}{8} \sum_i \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\beta}^2 \partial u_{i\gamma}^2} \right)_{eq} \quad (3)$$

where k_B is the Boltzmann constant, k , γ , γ_1 and γ_2 are the crystal parameters depending on the structure of crystal lattice and the interaction potential between particles at lattice knots, φ_{i0} is the interaction potential between i th particle and 0th particle, $u_{i\beta}$ is the displacement of i th particle from equilibrium position in the direction β ($\beta, \gamma = x, y, z, (\beta \neq \gamma)$) and N is the number of particles per mole or the Avogadro number.

II.2. Theory of rotational specific heat at constant volume for molecular cryocrystals of nitrogen type

We describe the ordered phase of crystals of nitrogen type from [12, 13]. These calculations in analytic form permit to derive more clear relation between proposals for intermolecular potential and obtained physical results. For considered crystal group, the quadrupole interaction U_{qq} has the most important contribution to electrostatic

$$U_{qq} = \frac{3Q^2}{4R^5} \left[1 - 5(\vec{\omega}_2 \vec{n})^2 - 5(\vec{\omega}_1 \vec{n})^2 + 2(\vec{\omega}_1 \vec{\omega}_2)^2 + 3(\vec{\omega}_1 \vec{n})^2 + 3(\vec{\omega}_1 \vec{n})^2 (\vec{\omega}_2 \vec{n})^2 - 20(\vec{\omega}_1 \vec{n})(\vec{\omega}_2 \vec{n})(\vec{\omega}_1 \vec{\omega}_2) \right] \quad (4)$$

where $\vec{\omega}_1, \vec{\omega}_2$ are unit vectors orientating towards the molecular axis, \vec{n} is the unit vector orientating to the line connecting two quadrupoles, Q is the quadrupole moment and R is the distance between inertial centers of molecules. If ignoring the crystal field and in the approximation considered in [5], the potential energy U is a bilinear function of the

quadrupole moment and is the distance between inertial centers of molecules. If ignoring the crystal field and in the approximation considered in [5], the potential energy is a bilinear function of the quadrupole moment $Q^{\alpha\beta} = \omega^\alpha \omega^\beta - \frac{1}{3}\delta^{\alpha\beta}$. The Hamiltonian for the system of interaction rotators is the sum of the kinetic energy of rotational motion and the potential energy

$$H = -B \sum_{\vec{f}} \left(\frac{1}{\sin\theta_{\vec{f}}} \frac{\partial}{\partial\theta_{\vec{f}}} \sin\theta_{\vec{f}} \frac{\partial}{\partial\theta_{\vec{f}}} + \frac{1}{\sin^2\theta_{\vec{f}}} \frac{\partial^2}{\partial\varphi_{\vec{f}}^2} \right) + U. \quad (5)$$

$$U = \frac{1}{2} \sum_{\vec{f}, \vec{f}' \alpha\beta\gamma\delta} V_{\vec{f}\vec{f}'}^{\alpha\beta\gamma\delta} Q_{\vec{f}}^{\alpha\beta} Q_{\vec{f}'}^{\gamma\delta}; \quad (6)$$

$$U = \frac{1}{2} \left[\sum_{\vec{f}, \vec{f}' \alpha, \beta, \gamma, \delta} V_1(R_{\vec{f}-\vec{f}'} Q_{\vec{f}}^{\alpha\beta} Q_{\vec{f}'}^{\alpha\beta} n^\alpha n^\beta n^\gamma n^\delta) + \sum_{\vec{f}, \vec{f}' \alpha\beta\gamma} V_2(R_{\vec{f}-\vec{f}'} Q_{\vec{f}}^{\alpha\beta} Q_{\vec{f}'}^{\beta\gamma} n^\alpha n^\gamma) + \sum_{\vec{f}, \vec{f}' \alpha\beta} V_3(R_{\vec{f}-\vec{f}'} Q_{\vec{f}}^{\alpha\beta} Q_{\vec{f}'}^{\beta\gamma}) \right], \quad (7)$$

where $B = \frac{\hbar}{2I}$. I is rotational constant, is the inertial moment of molecule, \vec{f} is the number of lattice knot, \vec{n} is the unit vectors in the direction, $\vec{f} - \vec{f}'$, θ_f , φ'_f are polar and azimuthal angles determining the orientation of molecule at the knot \vec{f} and the parameters V_1 V_2 and V_3 depend on molecular and crystal constants [5].

Equations of self-consistent field are simply obtained by the variational principle Bogoliubov [15]. We write the Hamiltonian (7) in the form $H = H_0 + H_1$ where

$$H_0 = \sum_{\vec{f}} H_{\vec{f}kin} + \sum_{\vec{f}} H_{\vec{f}}^{\alpha\beta} Q_{\vec{f}}^{\alpha\beta}. \quad (8)$$

Here $H_{\vec{f}}^{\alpha\beta}$ is the kinetic energy of rotators, $H_{\vec{f}kin}$ is the self-consistent field, which is considered as the variational parameter and $H_1 = H - H_0$. Therefore, the free energy F satisfies the inequality

$$F \leq F_0 + \overline{H_1} \quad (9)$$

where F_0 is the free energy corresponding to the Hamiltonian H_0 and $\overline{H_1}$ denotes the mean value of H_1 according to the Gibbs assemble with the Hamiltonian H_0 . Minimizing the right part of (9) on $\overline{Q}^{\alpha\beta}$ we go to the following system of equations

$$H_{\vec{f}}^{\alpha\beta} = \sum_{\vec{f}' \gamma\delta} V_{\vec{f}\vec{f}'}^{\alpha\beta, \gamma\delta} Q_{\vec{f}'}^{\gamma\delta}. \quad (10)$$

If substituting (10) into (8), the free energy determined by the right part of (9) is the free energy calculated with the Hamiltonian

$$H_{eff} = \sum_{\vec{f}} H_{\vec{f}kin} + \sum_{\vec{f}\vec{f}' \alpha, \beta, \gamma, \delta} V_{\vec{f}\vec{f}'}^{\alpha\beta, \gamma\delta} Q_{\vec{f}}^{\alpha\beta} Q_{\vec{f}'}^{\gamma\delta} - \frac{1}{2} \sum_{\vec{f}\vec{f}' \alpha, \beta, \gamma, \delta} V_{\vec{f}\vec{f}'}^{\alpha\beta, \alpha\beta} \overline{Q}_{\vec{f}}^{\alpha\beta} Q_{\vec{f}'}^{\gamma\delta} \quad (11)$$

For the lattice Pa3 the solutions of SCF equation (10) have the form [5]

$$\overline{Q}_f^{\alpha\beta} = \left(\omega_f^\alpha \omega_f^\beta - \frac{1}{3} \delta_{\alpha\beta} \right) \eta, \quad \eta = \langle p_2 \cos \theta \rangle, \quad p_2 \cos \theta = -\frac{1}{2} + \frac{3}{2} \cos^2 \theta \quad (12)$$

$\langle p_2 \cos \theta \rangle$ is the mean value of $p_2 \cos \theta$ and η is the ordered parameter of system because ignoring zero vibrations at $T=0$ and $\eta = 1$ in the orientational ordered phase, $\cos^2 \theta = \frac{1}{3}$, $\eta = 0$. After substituting (12) into (11), we obtain the Hamiltonian for the system of rotators in SCF approximation. In the approximation of two first coordinative spheres and putting the wave function $\psi(\theta, \varphi) = \Theta(\theta) \Phi(\varphi)$ where $\Phi_m(\varphi) = (2\pi)^{-1/2} e^{im\varphi}$, $m = 0; \pm 1; \pm 2 \dots$ we find the equation as follows

$$-B \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \Theta(\theta) - \frac{m^2}{\sin^2 \theta} \Theta(\theta) \right] - U_0 \eta P_2 \cos(\theta) \Theta(\theta) = E_m \Theta(\theta); \quad (13)$$

where U_0 is the constant of molecular field. We consider a pseudoharmonic approximation. In the limit $U_0 \eta / B \gg 1$, $\theta = 0, \pi$, $\sin \theta = \theta$ and putting forward variables $v = \theta \sin \varphi$, $u = \theta \cos \varphi$ we can transform Eq.(13) into an equation describing two uninteractive harmonic oscillators

$$-B \left(\frac{\partial^2}{\partial U^2} + \frac{\partial^2}{\partial v^2} \right) \psi + \frac{3}{2} U_0 \eta (u^2 + v^2) \psi - U_0 \eta \psi + \frac{U_0}{2} \eta^2 \psi = E \psi. \quad (14)$$

Energy levels of the system in the pseudoharmonic approximation can write in the form

$$E_{m,n} = -U_0 \eta + \frac{U_0 \eta^2}{2} + \varepsilon(n + m + 1); \quad n, m = 0, 1, 2 \dots; \quad \varepsilon = \sqrt{6U_0 \beta \eta}. \quad (15)$$

From that, the free energy is equal to

$$\frac{F}{N} = 2T \ln 4 \sinh \frac{\varepsilon}{2T} - U_0 \eta + \frac{U_0 \eta^2}{2} \quad (16)$$

The appearance of factor 4 in logarithm relates with the degeneracy of states. Minimizing the free energy (16) on the ordered parameter η we obtain the condition of self-consistency

$$\eta = 1 - \frac{3B}{\varepsilon} \coth \frac{\varepsilon}{2T}; \quad (17)$$

this together with (15) set up a closed system of equations. After substituting (15) into (17), we obtain an expression relating temperature with given value of ordered parameter

$$\frac{\varepsilon_0}{T} = \frac{1}{\sqrt{\eta}} \ln \frac{1 - \eta + \frac{3}{2} \gamma_0 \sqrt{\eta}}{1 - \eta - \frac{3}{2} \gamma_0 \sqrt{\eta}}; \quad \varepsilon_0 = \sqrt{6BU_0}; \quad \gamma_0 = \frac{2B}{\varepsilon_0}. \quad (18)$$

From the expression of free energy (16) counting the condition (17) and the definition of specific heat at constant volume $C_v = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_v$ we obtain

$$\frac{C_v}{R} = \frac{1}{2} \frac{(\varepsilon/T)^2}{\sinh^2(\varepsilon/2T)} \left(1 - \frac{T}{\varepsilon} \frac{\partial \varepsilon}{\partial T} \right) = C_v^E \left(1 - \frac{T}{\varepsilon} \frac{\partial \varepsilon}{\partial T} \right). \quad (19)$$

So, the anharmonicity of initial system of rotators determined in the SCF approximation is expressed in clear dependence of ε on temperature. That gives a supplementary contribution to the Einstein specific heat C_v^E

III. NUMERICAL RESULTS AND DISCUSSION

In order to apply the above theoretical results to cryocrystals of nitrogen type, we use the Lennard-Jones potential

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]; \quad (20)$$

where $\frac{\varepsilon}{K_B} = 95,1K; \sigma = 3,708.10^{10}\text{m}$ for $\alpha - N_2$ $\frac{\varepsilon}{K_B} = 95,1K; \sigma = 3,708.10^{10}\text{m}$ for $\alpha - N_2$ $\frac{\varepsilon}{K_B} = 100,1K; \sigma = 3,769.10^{10}\text{m}$ for $\alpha - CO$ $\frac{\varepsilon}{K_B} = 235,6K; \sigma = 3,802.10^{10}\text{m}$ for $\alpha - N_2O$ $\frac{\varepsilon}{K_B} = 218,9K; \sigma = 3,996.10^{10}\text{m}$ for $\alpha - CO_2$ The dependence of the ordered parameter η on temperature for cryocrystals of N_2 type is presented in Tables 1-4 [5]. Values of parameters U_0 and B for these crystals are presented in Table 5. The dependence of the specific heat C_v on temperature for cryocrystals of $N - 2$ type is represented in Figures 1-4. In these figures, C_{vrot} is the specific heat C_v taking account of only molecular rotations from SCFM, C_{vvib} is the specific heat C_v taking account of only lattice vibrations from SMM, $C_{vrot} + C_{vvib}$ is the specific heat C_v taking account of both lattice vibration and molecular rotations from SCFM and SMM and C_{vexpt} is the specific heat C_v from the experimental data. In comparison with experiments, the specific heat C_v taking account of both lattice vibrations and molecular rotations gives better results than the specific heat C_v taking account of only lattice vibrations or only molecular rotations.

Table 1. The dependence of the ordered parameter η on temperature for $\alpha - N_2$

T(K)	0	10	15	20	24	28	30	32	34
η	0.8633	0.861	0.8544	0.8404	0.8244	0.8038	0.7916	0.7778	0.7621

Table 2. The dependence of the ordered parameter η on temperature for $\alpha - CO$

T(K)	10	20	30	36	42	48	52	56	58	60
η	0.909	0.906	0.894	0.883	0.869	0.851	0.836	0.818	0.808	0.797

Table3. The dependence of the ordered parameter η on temperature for $\alpha - N_2O$

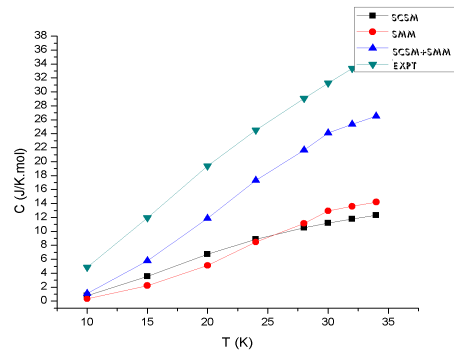
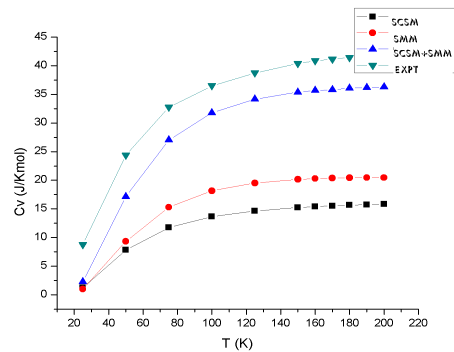
T(K)	25	50	75	100	125	150	160	170	175	180
η	0.986	0.983	0.978	0.972	0.964	0.955	0.951	0.946	0.943	0.941

Table 4. The dependence of the ordered parameter η on temperature for αCO_2

T(K)	0	25	50	75	100	125	150	160	17
η	0.9878	0.9859	0.9822	0.9775	0.9718	0.9880	0.9622	0.9590	0.9556
T(K)	180	190	200						
η	0.9619	0.948	0.9652						

Table 5. Values of parameters U_0, B for cryocrystals of N_2 type

Crystal	$\alpha - N_2$	$\alpha - CO$	$\alpha - N_2O$	$\alpha - CO_2$
$U_0 [K]$	325.6	688.2	5844.5	7293.8
$B [k]$	2.875	2.778	0.6059	0.56355

Fig. 1. Specific heat C_v of $\alpha - N_2$ Fig. 2. Specific heat C_v of $\alpha - CO_2$

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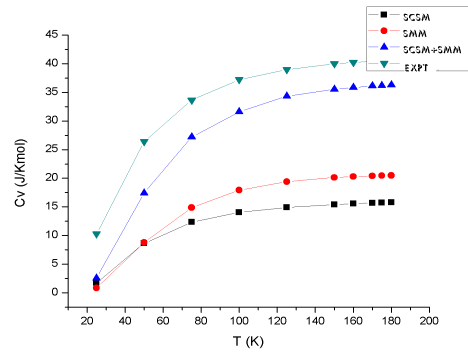


Fig. 3. Specific heat C_v of $\alpha - N_2$

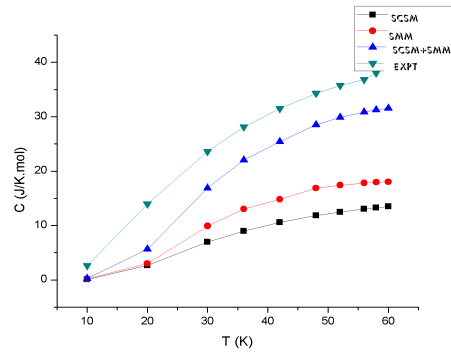


Fig. 4. Specific heat C_v of $\alpha - CO_2$

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