LATTICE DYNAMICS AND HEAT CAPACITY OF SOLID NITROGEN

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The heat capacity of solid nitrogen in α- and β- phases is analysed in the framework of theoretical approach taking into account all translational and orientational phonon modes, measured by the methods of neutron [1,2] and Raman [3,4] spectroscopy.

The elementary cell of solid nitrogen consists of 4 molecules, which can possess at low temperatures the 20 degrees of freedom: 3 translational acoustic, 9 translational optic and 8 orientational ones. Neglecting the effects of phonon dispersion and translational-orientational interactions we can approximate the spectral phonon density of states (DOS) by the expression

$$G(\omega) = \frac{3}{20}\frac{3\omega^2}{\omega_D{}^3} + \frac{1}{20}\sum_{i=1}^{9}\delta(\omega-\omega_i) + \frac{1}{20}\sum_{j=1}^{8}\delta(\omega-\omega_j)\ , \qquad (1)$$

where $\omega_D = k_B\Theta_D/\hbar$ is the cut-off acoustic (Debye) frequency and ω_i (ω_j) are the resonant translational (orientational) optic frequencies.

The molar lattice heat capacity is determined by the formula

$$C_{ph}(T) = 3nR\int_0^{\infty}\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{e^{\hbar\omega/k_BT}G(\omega)}{(e^{\hbar\omega/k_BT}-1)^2}\,d\omega\ , \qquad (2)$$

where n is the number of atoms, entering the chemical formula; R is the universal gas constant.

Using the complete set [5] of translational ω_i and orientational ω_j lattice modes measured in Γ-point at low temperatures

$$\omega_i = 46.8\ (A_u),\ 54.0\ (E_u),\ 48.6\ (T_u^-),\ 69.4\ (T_u^+)\ \ [cm^{-1}];$$
$$\omega_j = 32.1\ (E_g),\ 36.4\ (T_g^-),\ 60.0\ (T_g^+)\ \ [cm^{-1}],$$

accounting for their degeneration degree in accordance with number of dispersion curves calculated in Ref. 6 for each mode and the value of Debye temperature Θ_D = 83.5 K [5], we have calculated the phonon DOS (1) and heat capacity (2) without using any fitting parameters.

The results of the heat capacity calculations are presented in Fig.1 and they agree with the corresponding experimental data [7] better than in Ref. 6, where the interaction potential between N_2 molecules with a set of fitting parameters was used. The contributions to the heat capacity of the acoustic translational, optic translational and orientational phonon modes are now available and have been analysed. So, the knowledge of the phonon DOS, based on the measured characteristic lattice frequencies, can permit us to calculate the phonon energy, entropy and other thermodynamic functions of solid nitrogen. We have also separated the heat capacity jump in α-β transition region. As a result, its theoretical investigation can provide more detailed information on the critical fluctuations and peculiarities of the structural phase transition.

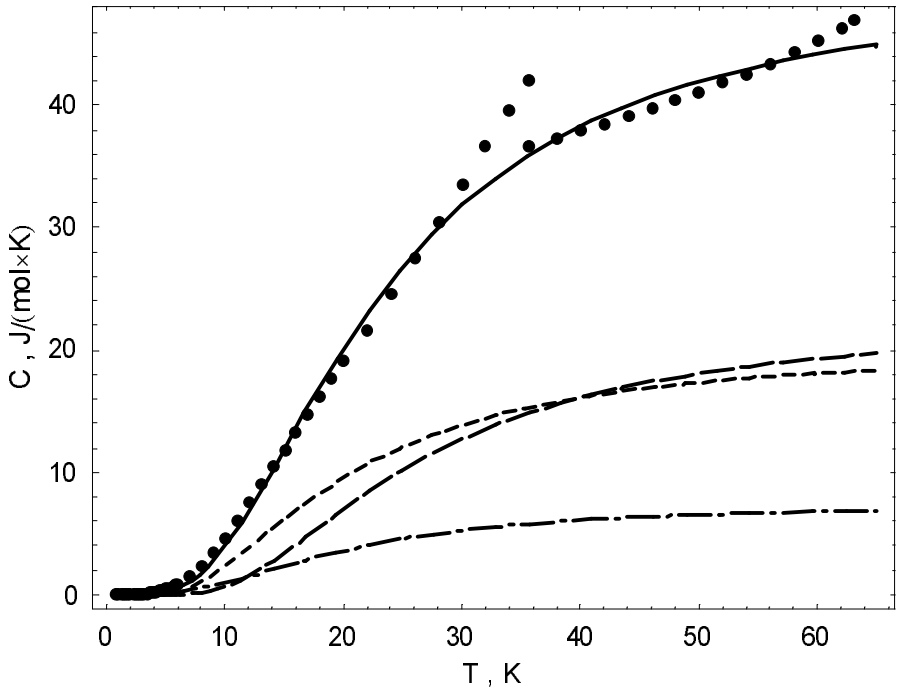

Fig. 1. Calculated (solid curve) heat capacity of solid nitrogen in comparison with measured one (points) [7]. The contributions of acoustic (dot-dashed curve), optic translational (long-dashed curve) and orientational (short-dashed curve) modes are demonstrated.

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