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Refractive indices and density of cryovacuum-deposited thin films of methane in the vicinity of the α–β-transition temperature

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Experimental studies of the effect of methane condensation temperature on the value of the refractive index and density of the resulting thin films are reported. The main unit of the installation is a high-vacuum chamber, which routinely operates at 10^{-8}–10^{-6} Torr. Measurements using a two-beam He–Ne laser interferometer in the vicinity of the methane phase transition temperature T = 20.4 K in the range of 14–32 K were carried out. It has been shown that in the vicinity of T = 20 K the temperature dependence of the refractive index undergoes an abrupt decrease with decreasing temperature. It is assumed that this gap is the result of the phase transition from the orientational disordered phase (α-phase) to the partially ordered phase (β-phase) of solid methane. The calculations of the polarizability of the methane molecules in the solid phase at two values of the deposition temperature T = 16 K and T = 30 K were performed using the Lorentz–Lorenz equation.

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1. Introduction

Solid methane has for nearly a century attracted the attention of researchers, and this interest continues unabated to the present, for strong and diverse reasons. The starting point of this long history of research was the discovery by Clusius (1929) [1] of the anomalous behavior of the heat capacity of methane at temperature T = 20.4 K. In 1959 James and Keenan [2] demonstrated theoretically that this anomaly may be explained as the phase transition from the high-temperature orientationally disordered phase of methane (α-phase) to the partially ordered phase at a temperature below T_c = 20.4 K (β-phase). Later it was discovered [3–5] that the β-phase is the intermediate state of solid methane towards the full orientation ordering phase (γ-phase).

The observed peculiarities in the properties of solid methane, both structural and other (i.e., optical, thermal, mechanical) are largely due to the nuclear spin relaxation processes and their influence on the rotational and translational subsystems of the methane crystal lattice. Study of these processes has been carried out either directly using structural methods [6,7] and the method of nuclear magnetic resonance [8–10], or indirectly, by examining the impact of conversion processes on the macroscopic characteristics of solid methane. This most clearly affects the vibrational spectra of methane in the range of translational and librational vibrations [11,12], as well as the thermophysical properties of methane, such as heat capacity [13,14], thermal conductivity [15], and density [16,17].

This article presents results of the studies of the influence of deposition temperature of methane on the refractive index and density values of the resulting thin films. In contrast to a rather large number of studies of equilibrium solid methane samples [6,16–18], here we demonstrate results obtained directly in the course of low-temperature deposition of the samples, which for this reason were essentially in a non-equilibrium state. Measurements were carried out in the vicinity of the phase transition temperature T = 20.4 K in the range of 14–32 K.

The transition from the orientationally disordered α-phase to the partially ordered β-phase and back changes the conditions of interaction between the external electromagnetic field and methane molecules, so as to change the contribution of the rotational subsystem to the process. This should affect the value of the refractive index, and the temperature de-