Elastic Properties and Phase Transitions in 1-Fluoroadamantane under Pressure

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The simplest diamondoids, adamantane ($C_{10}H_{16}$) and its derivatives, exhibit an orientationally disordered phase (plastic phase) and demonstrate rich polymorphic transitions upon changes in temperature or pressure [1]. 1-Fluoroadamantane ($C_{10}H_{15}F$) is one of the substituted adamantanes, and it has two polymorphs: one orientationally disordered phase at high temperature (HT) and a less disordered low-temperature (LT) phase [2]. However, recent work [3] demonstrated the existence of an intermediate phase of 1-Fluoroadamantane at low temperatures, investigated by temperature resolved second harmonic generation and X-ray powder diffraction.

In our work, we have studied the phase transitions in 1-Fluoroadamantane upon a temperature and pressure change by an ultrasonic method. The measurements of sound velocities and relative volume change were carried out on the high-pressure piston-cylinder setup in the pressure range 0–1 GPa and temperatures of 77–293 K, that allowed to calculate bulk and shear moduli and Poisson’s ratio. The measurements were performed by the pulsed ultrasonic method using $LiNbO_3$ plates as piezoelectric sensors with carrier frequencies of 5–10 MHz [4].

For 1-Fluoroadamantane, there is no data on the behavior under pressure; therefore, we compared the pressure dependences of the velocities of sound, volume, and elastic moduli with the adamantane, which we studied previously by the same ultrasonic method. Adamantane also exhibits a transition from an orientationally disordered phase to an ordered one upon increasing pressure or cooling. However, we found significant differences in the phase transitions of these two substances. While in adamantane at room temperature the transition occurs at 0.43 GPa with a jump in volume and shear modulus, but without an apparent change in the bulk modulus, the character of phase transition in 1-Fluoroadamantane is more complicated (Figure 1). This transition is a multistage and protracted. The initial orientationally disordered phase at 0.37 GPa transforms to another modification. In the pressure range of 0.37–0.46 GPa and 0.46–0.6 GPa, 1-Fluoroadamantane exists in an intermediate state, in which both the shear modulus and the bulk modulus are larger than in the initial phase. A transition to the next phase occurs at 0.6 GPa, and the behavior of elastic moduli in this new phase is similar to the tetragonal adamantane phase. One can assume that the modification of 1-Fluoroadamantane obtained at 0.6 GPa corresponds to the ordered low temperature phase, and the intermediate modification that exists at pressures of 0.37–0.6 GPa corresponds to the new intermediate phase found in work [3]. Experiments of warming 1-Fluoroadamantane from 77 to 293 K showed anomalies in the behavior of the amplitude of the ultrasonic signal at 175 and 220 K.

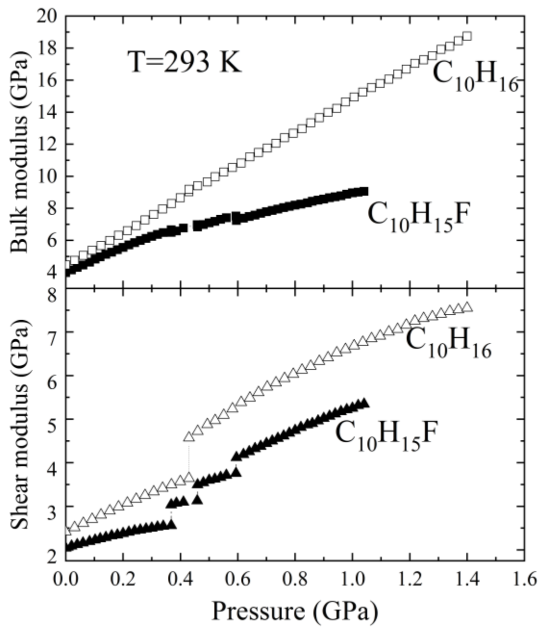

Figure 1. Bulk and shear moduli of adamantane ($C_{10}H_{16}$) and 1-Fluoroadamantane ($C_{10}H_{15}F$) at elevated pressure at room temperature 293 K

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