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Thermal transport in molecular crystals of 1-cyanoadamantane

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The heat capacity and thermal conductivity measurements of 1-cyanoadamantane samples were carried out for temperatures between 2 K and 225 K. Particular polymorphic states were obtained due to different thermal treatment made on samples. The heat capacity for both phases (monoclinic and glass-like) seems to be equivalent to each other below 75 K. The absence of linear temperature dependence of heat capacity at lowest temperatures for glass-like state results probably from insufficient measurement range. For monoclinic phase one can determine jump in heat capacity values at around 200 K, which is connected with the shift of phase transition between monoclinic and supercooled metastable cubic phase. Thermal conductivity measurements enabled to observe besides monoclinic and glass-like also few metastable states. Results obtained from monoclinic phase resembles the behavior of dielectric crystals with an exception of low temperature power dependency, $T^{2.69}$ instead of T^3. Glass-like phase results imitate curves typical for amorphous materials, only the characteristic plateau is shifted towards higher temperatures and broader than usual.

Key words: Thermal conductivity, phonon scattering, molecular disorder, glassy features

I. INTRODUCTION

Orientational glasses attract considerable attention as ones bearing a high number of similar features with canonical glasses. The origin of them is, that they are obtained from supercooled ergodic plastic phases instead of liquids[1]. Orientationally disordered phases generally appear for pseudoglobular molecules and display high-symmetry lattices with intrinsic disorder of molecules concerning orientational degrees of freedom. In that way orientational glasses might be considered as simplified models of ordinary structural glasses. Virtually any disordered state when quenched should give rise to a glassy state in which the original disorder has been frozen in. For plastic crystals, the low-symmetry molecular units forming the crystals are submitted to the high symmetry lattice and a large set of molecular orientations appear for simulating the symmetry of the crystallographic site. Although the number of materials exhibiting such disorder is small, few results have been reported [2].

We believe that investigations of two fundamental thermodynamic properties, thermal conductivity and heat capacity, may provide better insight into thermal behavior of disordered molecular systems.

1-cyanoadamantane [1-cyano-tricyclo[3,3,1,1]decane] is obtained from adamantane by substitution of hydrogen atom with a cyano group. Below the melting point (T_m=458 K) orientationally disordered plastic phase occurs with face-centered-cubic (*Fm3m*), where the molecular long axes are randomly distributed around the six orientations corresponding to the six crystallographic directions <001>. On further cooling (below 280 K) orientational order appears as monoclinic phase with space group C2/m. On contrary the glass-like state is observable only below 170 K. From literature one could expect the presence of metastable states [4].

II. EXPERIMENTAL

1-cyanoadamantane was purchased from Sigma-Aldrich® with purity 97% and was used as provided. The original form of the sample was powder and was transformed into convenient, measurement enabling shape by means of mechanical pressing, with power of 1500 kg cm^{-2}. The final form was cylindrical, 5mm in diameter. Thermal transport was characterized by carrying out heat capacity and thermal conductivity measurements. The first one were investigated using the Physical Property Measurement System (PPMS) from Quantum Design Inc. in Heat Capacity Option. The values of the heat capacity are determined by the two tau model [6]. Accuracy of the experiment was better than 1%. The thermal conductivity measurements were performed using specially designed bath cryostat, using the uniaxial stationary heat flux method [7]. The statistical error was kept below 3% for the whole temperature range, but the upper error bound (≈10%) mostly arises from the measurement of the sample geometrical parameters.

III. RESULTS & DISCUSSION

The heat capacity results are displayed od fig. 1. The sample was cooled from room temperature down to 2 K at the rate of ≈ 3 K min^{-1} and the heat capacity of the so-obtained monoclinic phase was measured on heating. Further, after Yamamuro et al. [8] the sample was submitted an additional 20h annealing just below the transition point, what resulted in a emergence of a completely ordered state. The data obtained for both phases exhibit no essential distinction at the low temperature range (see left upper inset). In this region heat capacity should pursue the T^3 Debye law, which is fulfilled. The slight deviation ($T^{3.15}$ for the ordered and $T^{3.36}$ for the monoclinic one) reflects only the difference between particular samples. For the disordered phase one could expect a lowest-temperatures linear dependency, which was unfortunately not covered by the set-up used at this experiment. At about 200 K for the results obtained in the monoclinic phase we observe a jump in heat capacity value (see right inset). This sudden change is connected with the shift of the phase transition between the monoclinic and the supercooled metastable cubic phase (the glass-like). On the contrary the results from the ordered phase are not influenced by the former presence of the phase transition at that temperature.

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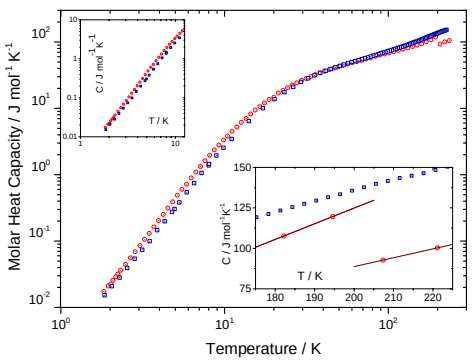

FIG. 1 (color online) Molar heat capacity of the monoclinic (red circles) and ordered (blue squares) phases of 1-cyanoadamantane in temperature dependency in a log-log scale.

The results of thermal conductivity measurements are presented in Fig. 2 in a double logarithm scale. While collecting the data we observe few metastable states, from which only two are reported here.

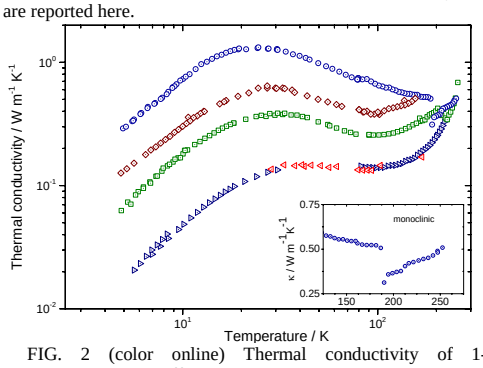

FIG. 2 (color online) Thermal conductivity of 1-cyanodamantane in different phases: blue circles – monoclinic, wine diamonds, green squares, navy/red triangles –metastable states

Experiment on the monoclinic phase were carried out on heating after slowly cooling of the sample from room temperature down to 4.2 K. The temperature dependence resembles the typical behavior of dielectric crystals with small deviation. At low temperatures thermal conductivity increases with $T^{2.69}$, which is not that far from standard T^3 [9]. Lowering of the power of the temperature dependence might be caused by the defects present in the samples, which give rise to number of phonon scattering centers. Increase of the thermal conductivity is followed by the maximum, at ≈ 24 K, where the dominant scattering mechanisms changes from that on grain boundaries/defects at low temperatures to U-processes at high temperatures. According to Leibried-Schlömann 1/T law at this region we can approximate our data [10]. With the temperature increase, at about 188 K a sudden drop of the thermal conductivity value emerges, which is connected, like in the heat capacity results, with the phase transition point between the monoclinic and the supercooled metastable cubic phase. However, in this case, the presence of the phase transition is already seen over 10 K lower than in heat capacity measurements. The sensitivity of the thermal conductivity experiments is also evidenced by the following increase of the coefficient value. The thermal conductivity curve with the lowest values was obtained after quenching the sample. The data resembles the typical temperature response of a disordered crystal [11]. At low temperatures thermal conductivity increases like $T^{1.96}$, which is almost overlapping with expected T^2, then a plateau takes place. A small anomaly would be the shift towards higher temperatures, it starts above 30K, and the broadening of the region, where it occurs. With increase of the temperature thermal conductivity also increases. This unusual phenomenon is connected with the ferroelectric structure of 1-cyanoadamantane [4]. At this region the intrinsic ordering has a predominant contribution.

IV. CONCLUSIONS

The thermal transport investigations on polymorphic states of 1-cyanoadamantane provide new information about phonon scattering mechanisms present in those materials. By differentiating thermal history made on samples it was possible to examine both disordered, ordered as well as metastable phases of 1-cyanoadamantane. It was shown that the main contribution to thermal transport mechanism has the scattering on grain boundaries and defects, which in some temperature regions is significantly predominating over other processes. As for heat capacity results an attempt will be made, to expand the investigated temperature range down to 0.3 K, in search of linear temperature dependency for the disordered phase.The results reported here give the opportunity for further studies on thermal transport mechanisms present in this class of disordered materials.

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