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Thermal conductivity of solid methane

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The thermal conductivity K of solid methane was measured within the temperature range of 1.2–25 K, using the steady-state method. The results obtained revealed an existence of the strong phonon scattering mechanisms connected with rotational excitation of the methane molecule. The dependence of thermal conductivity on the spin-nuclear distribution of methane molecules was observed. [S0163-1829(97)01502-6]

Solid methane is representative of a small group of molecular crystals (^{3}He,^{4}He,H_2,HD,D_2), which exhibit quantum effects. The quantum character of the crystals may appear in translational particle dynamics and/or in their rotational motion. Among the materials mentioned, methane is the only one for which the quantum character is associated exclusively with the rotational subsystem. On the other hand, characteristics of translational motion of methane puts it into the group of classic crystals. This unique nature of solid methane resulted in recent years in extensive theoretical and experimental investigations (see, for example, Ref. 1, and references therein).

Solid methane under equilibrium vapor pressure exists in two crystalline modifications. At 90.7 K it becomes solid in the orientationally disordered phase with the fcc structure—so-called plastic phase (phase I), where all molecules occupy O_h sites. At 20.4 K one observes the transition to the low-temperature cubic phase (phase II) containing eight sublattices. Six of them are related to the orientational order of methane octopoles occupying D_{2d} sites and forming an antiferrorotational structure. In the two remaining sublattices methane molecules occupy O_h sites, are dynamically disordered, and behave like weakly bound quasifree rotators.[2–4]

Depending on the total nuclear spin $I=0$; 1; 2, the methane molecule may exist in one of the three spin-nuclear modifications: E, F, or A, respectively.[2] At high temperatures, the equilibrium ratio of E:F:A amounts to 2:9:5. With decreasing temperatures, the ratio changes as a result of nuclear-spin conversion processes.

Relaxation rate depends on the molecule symmetry in the crystal. For the ordered sublattices relaxation time is of the order of 1 h, whereas for the disordered ones it is close to 100 h.[5–8] Introduction of impurities into the crystal may result in the acceleration of conversion processes. The ratio of E:F:A up to 20 K only slightly differs from that at high temperatures. At low temperatures all molecules appear in modification A.

A small moment of inertia caused by external hydrogen atoms, the fact that predominant anisotropic contribution into intermolecular interaction causes mainly a rise to the octopole-octopole interaction, and, finally, the conversion of nuclear spins, all engender quantum effects in the physical properties of solid methane. Specific-heat examination revealed the I-II phase transition[9] and allowed for calculation of the zero entropy.[10,11] Thermal-expansion measurements showed an anomaly resulting from the nuclear-spin conversion.[12–16] Based on NMR, Raman spectroscopy, neutron scattering, x-ray diffraction, and other experiments,[5,17–22] the following parameters were obtained: nuclear-spin conversion rates, tunneling splittings of librational energy levels, correlation times for molecular reorientation, site symmetries, and others. The evidence for the existence of nearly-free rotators in the phase II was also obtained. A number of theoretical papers were devoted to the methane phase transition theory,[2] libron and rotational spectra of methane molecules,[23,24] as well as to the crystal-field dependence of the rotational spectrum.[25,26]

Few papers were concentrated on the heat transport in solidified methane and, moreover, no literature data are available concerning these phenomena at temperatures below 18 K. Gerritsen and van der Star[27] examined thermal conductivity of solid methane in the phase-transition region, and observed the λ-type anomaly resembling that characteristic of the specific heat.[9] Manzhelii and Krupskii,[28] examining the phase II, found a bell-like anomaly in $K(T)$ dependence at ~50 K. This effect was interpreted by Yasuda[29] as an influence of correlations among molecular rotation axes on the phonon scattering.

The aim of the present paper was to investigate the thermal conductivity of the low-temperature phase of methane as well as of the phase-transition region and the influence of the spin-nuclear conversion on thermal conductivity. The measurements of thermal conductivity were carried out by the stationary heat flux method within the temperature range of 1.2–25 K, applying a measuring system presented in Ref. 30. A glass ampoule of 67 mm height, inner diameter of 8.65 mm, and wall thickness of 1.1 mm was used. The temperature of the sample and the temperature gradient were determined with two germanium thermometers attached to the ampoule wall separated 37.3 mm from each other. The random error of the thermal conductivity measurements did not exceed 3%. Gaseous methane used for the sample preparation had the following impurity concentrations CH_3D—1.76%, CHD_3—0.12%, N_2—0.04% and O_2—<0.01%.

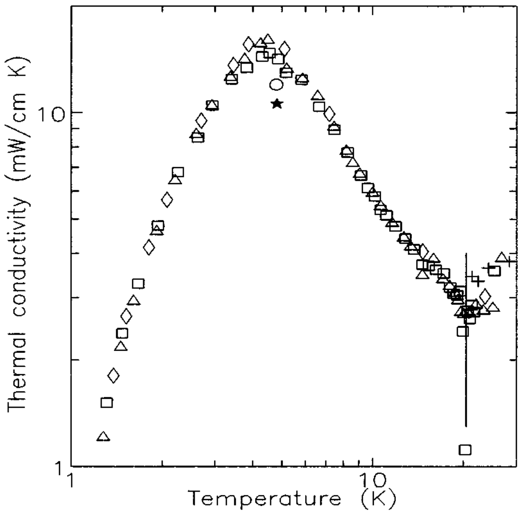

FIG. 1. Temperature dependences of thermal conductivity of solid methane: □ indicates measurements during cooling; △ indicates measurements during heating; + indicates data taken from Ref. 28; ★ indicates measurement at 4.8 K after cooling from $T=25$ K; ○ indicates measurement at 4.8 K after heating from $T=1.5$ K (see text for details). The vertical line indicates the temperature of the phase transition.

The crystal was grown from the vapor phase at 88 K, i.e., slightly below the triple-point temperature (90.7 K). Crystal growth rate amounted to 1.6 mm/h. Gas pressure during the growth process was constant and equal to 8.5 kPa. After growing the crystal was annealed at 69 K during 48 h with the temperature gradient along the sample of 1 K. Cooling of the crystal down to 40 K and subsequently to 25 K was performed with a rate of 1 and 1.5 K/h, respectively. The crystal obtained was transparent with a tiny defect in the form of a chain of small bubbles.

Thermal conductivity measurements were performed while cooling from 25 K down to 1.2 K. Subsequently, the sample was aged at 1.2 K for 40 h. Finally, the same measurements were conducted *versus* increasing temperature. The time in which the crystal reached thermal equilibrium during measurements ranged between 4 h at 20 K to 1 h at 8 K and below this temperature.

The results of thermal conductivity measurements of solid methane obtained for two samples were presented in Fig. 1. The data observed above the phase-transition temperature agree with those reported earlier.[28] In this region thermal conductivity depends weakly on temperature. The time of passage across the phase-transition region (20.5–20.3 K) amounted to 8 h. With temperature decreasing slightly below the phase transition (20.4 K), the thermal conductivity decreased abruptly and subsequently returned to the previous value at 19 K. With the further decrease of temperature, the value of the thermal conductivity increases up to 4.5 K and subsequently falls down. The maximum value is equal to $K_{\max}=11$ mW/cm K. The latter value is markedly low in comparison to that characteristic of the solid noble gases argon[31] or krypton[32] and also molecular crystals like O_2,[33] N_2,[34] and hydrogen isotopes.[35,36] Temperature dependence of the thermal conductivity over a range from $T_{\max}$ up to the phase transition is of the T^{-1} type. Below $T_{\max}$ it changes to $K(T) \propto T^2$.

The low value of the thermal conductivity coefficient at the maximum temperature and the lack of the exponential dependence of $K(T)$ for $T>T_{\max}$ are remarkable. In the case of the low-temperature phase, molecules may be located either in D_{2d} or O_h sites. Those methane molecules which occupy the D_{2d} sites exhibit a libron spectrum. This spectrum is characteristic of a group of the low-energy levels below 1 K, i.e., minimum experimental temperature. There is a gap of ~63 K between the low-temperature branch of the spectrum and the next group of energy levels. The high-temperature branch of the spectrum weakly influences the thermal conductivity in the maximum region. On the other hand, the rotational spectrum of the molecules occupying the O_h sites is more complex in the low-energy region and exhibits the nearly constant level density with a gap of 7 K. Most probably, the scattering on those rotational excitations leads to the observed temperature dependence of the thermal conductivity for solidified methane.

Results of thermal conductivity measurements obtained during heating from 1.2 up to 25 K are the same as those found while cooling, except in the vicinity of phase transition. Namely, no increase of $K(T)$ was observed before the phase-transition region, 19–20.4 K.

The λ-type anomaly reported in Ref. 27 at the phase-transition region was not confirmed by our measurements. We think that effect observed by Gerritsen and van der Star was influenced by their measurement method. Probably, they measured the value of the thermal conductivity coefficient while the temperature of the phase transition drifted between the temperatures of gradient thermometers. Therefore, the as-measured value of the temperature gradient was smaller than the real value, hence these authors observed a λ-like peak in the region of the phase transition. In our measurements we avoided this situation, determining the value of the thermal conductivity coefficient in regions just below and above the transition. It should also be noted that the K values behind the phase-transition region $T>20.4$ K (where the eventual impurities do not influence considerably the value of the thermal conductivity coefficient) obtained by Gerritsen and van der Star[27] are several times lower. We are of the opinion that these discrepancies were caused by a large systematic error resulting from the incorrect estimation of sample dimensions.

In order to explain the influence of conversion of methane molecules on the thermal conductivity, the crystal was cooled from 25 K down to 4.8 K in a period of 2 h and the thermal conductivity was measured (see Fig. 1). Subsequently it was cooled down to 1.5 K and kept at this temperature during 12 h. Next it was warmed during 1 h up to 4.8 K and the measurements were repeated. As a result of that procedure, a difference of ~10% in the value of K at 4.8 K was found. We think that this is caused by a change of the distribution of spin-nuclear modification.

Concluding, we would like to state that the thermal conductivity dependence of solid methane below maximum is proportional to T^2. A low value of the maximum, as well as the lack of exponential dependence above $T_{\max}$, result from the presence of strong phonon scattering mechanisms associated with rotational excitations of methane molecules. An influence of the spin-nuclear conversion on thermal conductivity of the solid methane was observed. These investigations are being continued and their results will be reported in the near future.

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