

# Orientational isotopic effects in the thermal conductivity of CH<sub>4</sub>/CD<sub>4</sub> solid solutions

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The thermal conductivity of (CH<sub>4</sub>)<sub>1-c</sub>(CD<sub>4</sub>)<sub>c</sub> solid solutions with  $c = 0, 0.03, 0.065, 0.13, 0.22, 0.4, 0.78,$  and 1.0 has been measured in the region of existence of three orientational phases: disordered (phase I), partially ordered (phase II) and completely ordered (phase III). The temperature range is 1.3–30 K. It is shown that the thermal conductivity has different temperature dependences  $\kappa(T)$  in these phases. Its value increases with the degree of the orientational order in the phase. In phase I the thermal conductivity is independent of  $c$  and weakly dependent on  $T$ . The impurity effect in  $\kappa(T)$  is much stronger in the low-temperature part of phase II than in phase III. As the concentration  $c$  grows, the  $\kappa(T)$  curve of phase II approaches the dependence  $\kappa(T)$  typical of phase I. There is a hysteresis in the vicinity of the II $\leftrightarrow$ III phase transition. In phase III the impurity effect in  $\kappa(T)$  can be considered as phonon scattering at rotational defects developing due to the difference between the moments of inertia of the CH<sub>4</sub> and CD<sub>4</sub> molecules. The obtained dependences of thermal conductivity on temperature and concentration can be explained qualitatively assuming that the dominant mechanism of phonon scattering is connected with the interaction of phonons with the rotational motion of the molecules in all of the three orientational phases of the CH<sub>4</sub>–CD<sub>4</sub> system.

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## Introduction

Crystalline methane, deuteromethane and their solid solutions are very interesting physical quantum objects: they undergo structural solid-state orientational transformations [1,2] and, besides, the rotational motion of their molecules can proceed as librations and as weakly hindered or free rotation. The strong isotopic effects observed in the properties of these substances [3] are first of all connected with the rotational degrees of freedom, the quantum statistics of nuclear spins and the weak anisotropic molecular interaction. The phase transformations from the orientational disorder (phase I) to the partial orientational order (phase II) and then from phase II to the completely orientationally ordered phase (phase III) occurs under equilibrium vapor pressure in

pure CD<sub>4</sub> and its concentrated solutions with CH<sub>4</sub>, Kr, Xe and at  $P > 200$  bar in pure CH<sub>4</sub>. Deuteration considerably affects the dynamics of the molecules in the orientationally ordered phases of solid methane, mainly because the rotational constant  $B = \hbar^2/2Ik_B$  ( $I$  is the moment of inertia) of CD<sub>4</sub> ( $B = 3.75$  K) is half as high as that of CH<sub>4</sub> ( $B = 7.5$  K). Under equilibrium vapor pressure solid CH<sub>4</sub> experiences one phase transition from orientationally disordered phase I (plastic phase with cubic symmetry) to phase II with partial orientational order, at  $T_{I-II} = 20.4$  K. Apart from phases I and II with  $T_{I-II} = 27.4$  K, CD<sub>4</sub> can have a state with a complete orientational order (phase III). Its structure (orthorhombic symmetry group  $Cmca$ ) is not cubic and is very close to the structure of phase II [4]. The orientational

phase transformation at  $T_{II-III} = 22.1$  K is a first-order phase transition with a volume jump of 0.63% [5,4], which is much larger than that during the I–II phase transition. The considerable difference between the rotational constants, different total nuclear spins of the  $CD_4$  and  $CH_4$  molecules and the weak molecular field are the factors that generate strong orientational fluctuations in the vicinity of the phase transition temperature [6,7]. In solid  $CH_4$ – $CD_4$  solutions phase III can exist under the equilibrium vapor pressure in a wide range of temperatures at  $CH_4$  concentrations  $c$  above 0.15 [2].

In phase I the molecules occupy the sites of the fcc lattice. They possess high orientational mobility: the thermal orientational fluctuations whose frequency increases with temperature provoke random jump-like reorientations of the molecules (rotational diffusion). The rotational diffusion of  $CH_4$  molecules occurs when the temperature decreases down to the point of the orientational phase transition ( $T_{I-II} = 20.4$  K). The orientational fluctuations can be viewed as random rotational moment through which the neighboring atoms and molecules influence the molecule. The fluctuations are usually of the order of  $k_B T/B$  [3].

The structure of phase II in  $CD_4$  was predicted by James in 1958 [8] and detected experimentally by Press in 1973 [9]. In contrast to  $CD_4$ , there is no direct unambiguous information about the structure of  $CH_4$ . However, the experimental evidence shows that in both substances phases II have identical crystalline structures with the space group  $Fm3c$ . The unit cell of phase II consists of 32 molecules and 8 sublattices. In six sublattices the molecules are orientationally ordered in opposite directions. In the other two sublattices the anisotropic contributions of the nearest molecules to the molecular field are counter balanced and the molecules located at these sites behave as weakly hindered rotators. The symmetry of the site is  $O_h$  for free rotators and  $D_{2d}$  for orientationally ordered molecules. The molecules at the  $O_h$  sites are weakly hindered rotators. The structure of their low-lying energy levels (the splitting is about 12 K) is quite similar to that of a free molecule. The molecular octupole interaction in phase II of  $CH_4$  ( $CD_4$ ) is not strong enough to align all the molecules in the preferred directions. The interactions cannot suppress the large oscillations of the  $D_{2d}$  molecules about their equilibrium orientations in the potential wells. This property sets methane off from other molecular crystals.

The structure of phase III has the spatial symmetry  $Cmca$  [4]. It has a tetragonal primitive lattice with  $c = 11.708$  Å and  $a = b = 8.187$  Å (this corresponds effectively to 1.0 % of tetragonal distortion). The unit cell contains 16 molecules. The arrangement of the carbon atoms is nearly the same as in the fcc lattice. The frustration effects generated by the ordering of tetrahedral molecules prohibits a complete orientational order in the fcc lattice.

In phase III, unlike phase II, eight of 16 molecules in the unit cell change their orientations drastically: four molecules rotate by  $90^\circ$  and four molecules become orientationally ordered. The remaining eight molecules (ordered in phase II) practically hold their initial positions and orientations, the deviation being only  $5.2^\circ$ . In phase II ( $4m2$ ) the deviation of the most symmetrical orientation is  $\pm 4.5^\circ$ . The libration amplitude is about  $15^\circ$  at all the sites at  $T = 18$  K [4].

On transformation from phase I to phase III, the  $CD_4$  (or  $CH_4$  under pressure) molecules change from complete orientational disordering (phase I) to a partially ordered state (phase II) and finally to complete ordering (phase III). The molecular rotation changes drastically: from random orientational wandering (rotational diffusion) caused by the thermal orientational fluctuations (phase I) to anharmonic librations about the ordered orientations (phase III). Near the phase transitions temperature the heat capacity exhibits anomalous features and considerable entropy effects [10] which account for intensive orientational motion of the molecules. In phases II and III the thermal orientational fluctuations provoke the molecules to hop between the neighboring orientations. The frequency of these reorientations decreases as the temperature lowers and the fluctuations attenuate. The main features of phases II and III are visualized in the rotational spectrum. It is structured at low temperatures (with one or more frequencies of coherent tunnel rotation), broadens with increasing temperature and attains the shape typical for no coherent thermoactivated orientational motion (random reorientations [3]).

The thermal conductivity  $\kappa$  is an useful physical property in investigations of molecular substances [11]. By measuring  $\kappa$  as a function of temperature, it is possible to characterize the orientational phases. For dynamically disordered phases and orientational glasses  $\kappa$  has been found to be almost independent of temperature (weak increase with temperature [11–13]). In the orientationally ordered phases  $\kappa$  decreases exponentially as a function of temperature and approaches  $T^{-1}$  near or above the Debye temperature [14]. A deviation from  $T^{-1}$  is observed when the mean free path of the thermal phonons is at its allowable minimum (about the size of the unit cell) [14].

Since the rotation of  $CH_4$  molecules and the translational vibrations of the lattice are interrelated, thermal conductivity is a very sensitive tool of investigating the orientational phase transitions in methane [15–17]. In our experiments the thermal conductivity was investigated in different orientational phases of  $(CH_4)_{1-c}(CD_4)_c$  solid solutions in a wide interval of concentrations.

In deuteromethane the increase in temperature from absolute zero can change the rotational motion of the initially (at  $T = 0$ ) ordered molecules as follows:

- zero-amplitude librations enhance up to anharmonic librations (phase III);
- the molecules undergo random jump-like reorientations (phase II);
- the frequency of reorientations increases up to rotational diffusion (phase I).

The investigation of the intra- and interphase evolution of the thermal conductivity can provide new information about the molecular dynamics in the cause of solid-state transformations.

### Experimental results

The experiments were carried out using the home-designed setup described earlier [18]. The thermal conductivity was measured in the temperature range from 1.3 to 30 K by the steady-state heat-flow method. The temperature and its gradient along the sample were measured with two germanium thermometers separated by 12 mm from each other. The relative error of the thermal conductivity measurements did not exceed 6%. The random error was no more than 2%. The temperature gradient between the two thermometers was about  $0.03T$ . The procedure of growing and cooling the  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  crystals is described elsewhere [17]. Here we report new experimental data on the thermal conductivity of  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  at  $c = 0.4, 0.78$  and  $1.0$  and analyze the dependences of thermal conductivity on temperature and  $\text{CD}_4$  concentration. Thermal conductivity data for the  $\text{CH}_4\text{--CD}_4$  system have been published in brief reports [17,19,20]. The thermal conductivities of  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  are shown in Fig. 1 (weak solutions with  $c = 0, 0.03, 0.065$ , and  $0.13 \text{ CD}_4$ ) and Fig. 2 (concentrated solutions with  $c = 0.22, 0.4, 0.78$ , and  $1.0 \text{ CD}_4$ ). The dependences of thermal conductivity on  $\text{CD}_4$  concentration in phases I, II and III are shown in Fig. 3.

The thermal conductivity of the  $\text{CH}_4\text{--CD}_4$  system is determined predominantly by the orientational order of the

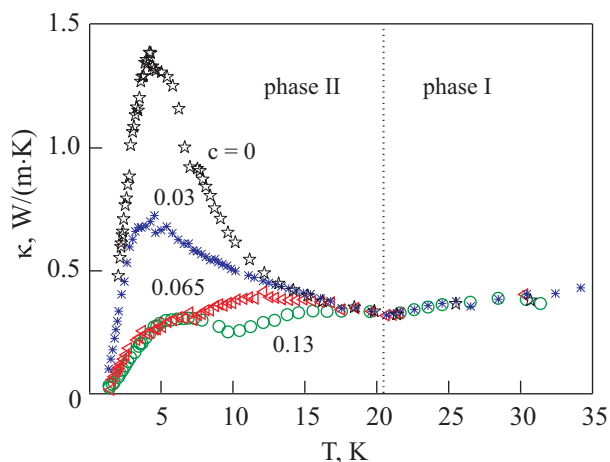


Fig. 1. Thermal conductivity of  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  for  $c = 0, 0.03, 0.065$ , and  $0.13$ . The dotted line is the temperature of orientational I–II phase transition for  $c = 0$ .

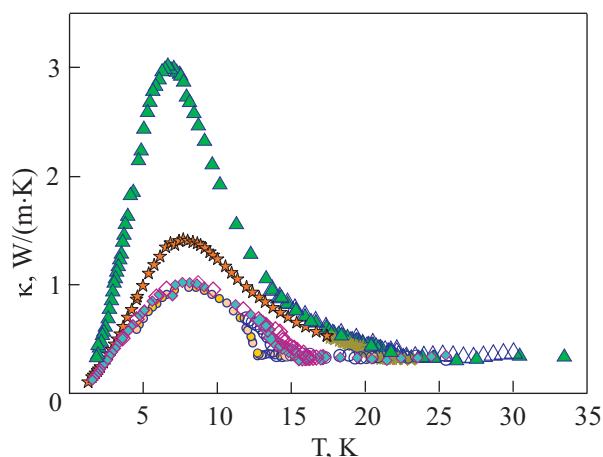


Fig. 2. Thermal conductivity of  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  for  $c = 0.22$  ( $\circ, \bullet$ ),  $0.40$  ( $\diamond, \blacklozenge$ ),  $0.78$  ( $\star, \blackstar$ ) and  $1.00$  ( $\triangle, \blacktriangle$ ) on increasing (open symbols) and decreasing (solid symbols) temperatures in the vicinity of the orientational phase transition II–III.

phase. It increases as the dynamical disorder (phase I) changes into partial (phase II) and then into complete orientational order (phase III). In the general case this behavior accounts for the attenuating anharmonic rotation at a growing degree of orientational ordering. This regularity is clearly illustrated by the impurity-caused isotopic effect in  $\kappa(T)$  and the jump in the concentration dependence of the thermal conductivity (Fig. 3) during the II–III phase transition. The impurity effect in  $\kappa(T)$  is much stronger in the low-temperature part of phase II than in phase III. As the concentration  $c$  increases, the curve  $\kappa(T)$  in the low-temperature part of phase II approaches the  $\kappa(T)$  of phase I. The impurity effect in the thermal conductivity of phase III can be interpreted as scattering of phonons at the rotational defects that develop due to the difference between the rotational constants of the  $\text{CH}_4$  and  $\text{CD}_4$  molecules. The behavior of  $\kappa(T)$  in the high-temperature part of phase II ( $c \geq 0.22$ ) is similar to that

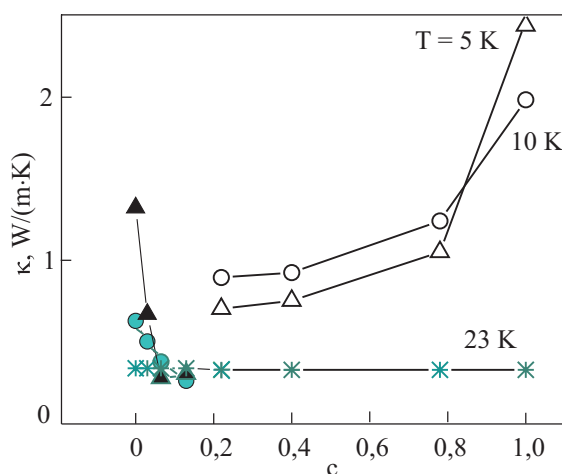


Fig. 3. Concentration dependence of the thermal conductivity of  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  for three different temperatures:  $T = 5$  ( $\triangle, \blacktriangle$ ),  $10$  ( $\circ, \bullet$ ) and  $23$  ( $\ast$ ) K. Open and solid symbols are data for phases III and II, respectively, and the symbols  $\ast$  are for phase I.

of phase I: the thermal conductivity is independent of the  $\text{CD}_4$  concentration and decreases very slowly with decreasing temperature ( $d\kappa/dT > 0$ ) down to the transition to the low-temperature phase II or to phase III where  $d\kappa/dT$  only changes sign. In phase II of pure  $\text{CH}_4$  and phase III of pure  $\text{CD}_4$   $\kappa(T)$  decreases exponentially with increasing temperature in the interval from 7 K to the temperature of the orientational transition.

The thermal conductivity has a hysteresis in the vicinity of the II–III phase transition [20]. Its width increases with the  $\text{CH}_4$  concentration. The smoothed thermal conductivities ( $c = 0.4$ ) in the hysteresis region are shown in Fig. 4. The marked points characterize the temperature behavior of phase transformation.  $T_2$  is the onset of phase III at lowering temperature,  $T_3$  specifies the moment when phase II disappears. At rising temperature phase II appears at  $T_4$  and phase III disappears at  $T_1$ . A quasi-stationary two-phase state is observed in the interval  $T_3 - T_1$ , where the thermal conductivity measured at the same temperature is independent of time (at least during 24 hours of observation). On changing from cooling to heating or vice versa, the curve  $\kappa(T)$  reverses in the  $T_3 - T_1$  interval and shows a weak dependence on temperature. The inverse  $\kappa(T)$  (dashed line in Fig. 4) is reversible if the temperature is varied within the hysteresis region, i.e., the curve is reproducible no matter whether the temperature is increasing or decreasing. At increasing concentration  $c$  the hysteresis of  $\kappa(T)$  shifts towards low temperatures and its  $T$  and  $\kappa$  ranges extend.

The new phase diagram of  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  with the specified parameters of the hysteresis ( $T_1, T_2, T_3, T_4$ ) is shown in Fig. 5. It is in good agreement with published data [1,2,10] and provides additional information about the region of existence of the heterogeneous state. It is of fundamental importance that the heterogeneous state is

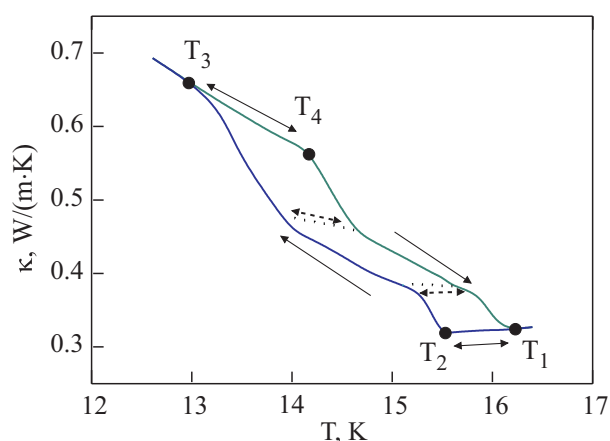


Fig. 4. Hysteresis of the thermal conductivity of  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  for  $c = 0.4$  in the vicinity of orientational phase transition II–III. Points  $T_2, T_3$  (decreasing temperature) and points  $T_4, T_1$  (increasing temperature) correspond to the beginning and the finish of the phase transition. Arrows show the direction of temperature change.

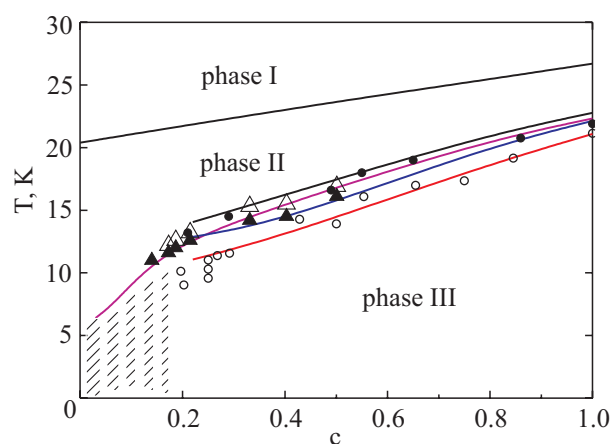


Fig. 5. Part of the phase diagram of  $\text{CH}_4$ – $\text{CD}_4$  solid solution. We show here the temperature of the phase transition II–III in dependence on concentration of  $\text{CD}_4$  in the mixed crystal  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  obtained from a fixed thermal conductivity (solid lines), from x-ray scattering ( $\circ$ ) [1], from NMR ( $\triangle, \blacktriangle$ ) [2] and from heat capacity ( $\bullet$ ) [10] measurements. The shaded area contains local orientational ordered regions of phase III.

quasistationary and stable on the reversal of temperature. This state can be considered as a mixed two-phase state of coexistence of phases II and III. In this region  $\kappa(T)$  is actually an effective thermal conductivity  $\kappa_{\text{eff}}(T)$  determined by the relation between the thermal conductivities of the two phases. The curve  $\kappa_{\text{eff}}(T)$  can be influenced to some extent by the complex spatial structure of the mixed state which can vary depending on the concentrations of the phases.

The diagram of the orientational phases is shown in Fig. 5. The II–III phase boundary was drawn on the basis of the  $\kappa(T)$  behavior. The shaded region shows possible local formations of phase III in phase II. Such zones with orientationally ordered molecules form along the line extrapolated from the dependences of the II–III transition temperatures on  $\text{CD}_4$  concentrations. The curve  $\kappa(T)$  has a kink at the transition point, which is particularly distinct at  $c = 0.13$  and decreases as the concentration  $c$  lowers. In the region with phase III inclusions, the thermal conductivity  $\kappa(T)$  is influenced by the temperature prehistory of the sample. The nuclear spin conversion of  $\text{CH}_4$  molecules causing relaxation of  $\kappa(T)$  [21,22] has little effect on  $\kappa(T)$ .

In terms of quality, the change of the thermal conductivity versus sample composition follows general expectations: the thermal conductivity of the solutions is lower than that of pure crystals. An increase of the isotopic admixture causes lowering of the thermal conductivity, which is most prominent at the maximum in the temperature dependence. However, the dependence of the thermal conductivity on temperature measured for samples containing 0.065 and 0.13  $\text{CD}_4$  diverges from that observed for other isotopic solid solutions, see, e.g., [23,24]. For these two concentrations of  $\text{CD}_4$  the maximum disappears

and the dependence resembles that known rather for «glassy» solids than the crystalline ones: initially, at the lowest investigated temperatures,  $\kappa(T)$  increases approximately as  $T^2$ , then the thermal conductivity saturates and, starting from 5–6 K up to the temperature of the phase transition, does not change within the accuracy of the experiment. The value of thermal conductivity within the plateau area amounts to 0.3 W/(m·K), which is consistent with values found for some glasses.

### Discussion

The obtained dependences of thermal conductivity on temperature and concentration in solid solutions can be explained quantitatively assuming that phonon scattering is governed predominantly by the interaction between the phonons and the rotational motion of molecules in three orientational phases of the CH<sub>4</sub>–CD<sub>4</sub> system. The  $\kappa(T)$  behavior in pure CH<sub>4</sub> and CD<sub>4</sub> is determined by the orientational dynamics at lowering temperature. The rotational motion of molecules in phase I can be interpreted as follows [25]. Each molecule by itself is a hindered rotator whose rotation in a short interval of time is randomly modulated by the neighboring molecules through a weak anisotropic molecular interaction. The rotation of the molecule at the site can be considered as a stochastic process disturbed randomly by the neighboring molecules which rotate randomly and independently of one another. The modulated hindered rotation is a source of additional phonon scattering.

At the point of the transition to the partially ordered phase there is a kink in the thermal conductivity curve. In the ordered phase the thermal conductivity passes through the maximum and then decreases with the lowering temperature. The initial increase of the thermal conductivity of the ordered phase of methane is due to the decrease of the number of phonons with the energy sufficient to interact with the scattering centers at lower temperatures. Its further decrease is due to the reducing density of thermal phonons which are scattered by the crystal boundaries and other defects.

The curve  $\kappa(T)$  measured on pure substances (CH<sub>4</sub> in phase II and CD<sub>4</sub> in phase III) can be described [17] by the expression based on the approximation of additivity of thermal resistance

$$\kappa(T) = \frac{\kappa_1(T)\kappa_2(T)}{\kappa_1(T) + \kappa_2(T)}, \quad (1)$$

where  $\kappa_1(T) = C_1 T^2$  and  $\kappa_2(T) = C_2 \exp(E/T)$ . Deuteration of CH<sub>4</sub> has a very little effect on the fitting parameters, which are  $C_1 = 0.08$  W/(m·K<sup>3</sup>) and 0.1 W/(m·K<sup>3</sup>) and  $C_2 = 0.08$  W/(m·K) and 0.14 W/(m·K) for CD<sub>4</sub> and CH<sub>4</sub>, respectively. The exponential growth of the thermal conductivity with lowering temperature in the low-temperature phase (phase II for CH<sub>4</sub> and phase III for CD<sub>4</sub>) corre-

sponds to thermally activated scattering of phonons by the rotational states against the background of phonon–phonon scattering (Umklapp process). The activation energies are  $E = 35$  K for CD<sub>4</sub> and 12 K for CH<sub>4</sub>. The transition from the nonactivated mechanism in phase I to the activated regime in phases II and III accounts for the change in the rotational motion. The librational motions of the ordered molecules are thermally activated and their amplitudes decrease with lowering temperature. It is natural that the activation energy is lower for CH<sub>4</sub> molecules than for the CD<sub>4</sub> ones (because of the different rotational constants of these molecules).

Traditionally, the temperature dependence of thermal conductivity is described quite accurately by the Debye–Pierls model of an isotropic solid. The model disregards the difference between the phonon modes of different polarizations

$$K(T) = \frac{k_B^4}{2\pi^2 \hbar^3 s} T^3 \int_0^{\Theta/T} \tau(x) \frac{x^4 e^x}{(1-e^x)^2} dx, \quad (2)$$

where  $k_B$  is the Boltzmann constant,  $\hbar$  is Planck's constant,  $\Theta$  is the Debye temperature,  $s$  is the mean sound velocity,  $x = \hbar\omega/k_B T$ , and  $\tau(x)$  is the effective relaxation time of the phonons participating in scattering. The normal phonon–phonon processes can be omitted from consideration because of their low intensity in CH<sub>4</sub> and CD<sub>4</sub> [26–28]. The inverse relaxation time (relaxation rate)  $\tau^{-1}(\omega)$  is a sum of the rates of all resistive processes of phonon scattering. The temperature dependence of the thermal conductivity of a molecular crystal is determined by the mechanisms of phonon scattering typical for crystals with no rotational degrees of freedom (Umklapp processes  $\tau_{U}^{-1}$ , boundary scattering  $\tau_B^{-1}$ , scattering at dislocations  $\tau_{dis}^{-1}$ , and point defects  $\tau_R^{-1}$ ) and by the additional mechanism allowing a coupling of the phonon gas and the rotational degrees of freedom (librations and/or rotation of molecules) of the molecular crystal.

The mechanism of the rotation–translation coupling is quite clear in the general case [29]. There is no theoretical model permitting a quantitative description of the thermal conductivity in different orientational phases of the crystal. It is known that the thermal conductivity of the orientationally disordered phase is little dependent on temperature. The experimental data on the low-temperature thermal conductivity of simple molecular crystals: H<sub>2</sub> [30], N<sub>2</sub> [31], CO [32], CH<sub>4</sub> [17,26], CD<sub>4</sub> [17], CO<sub>2</sub> [33], N<sub>2</sub>O [33,34], and others [35,36] describes only the general behavior of the thermal conductivity of the orientationally ordered crystal. The temperature dependence of the thermal conductivity of molecular crystal is identical to that of an atomic crystal with defects and can be described formally by the mechanisms typical of crystals

having no rotational degrees of freedom. The total relaxation rate  $\tau^{-1}(\omega)$  can be written down as

$$\tau^{-1}(\omega, T) = \tau_U^{-1}(\omega, T) + \tau_{\text{dis}}^{-1}(\omega) + \tau_R^{-1}(\omega). \quad (3)$$

In Eq. (3) the relaxation rate of the thermal activated U-processes is

$$\tau_U^{-1}(\omega, T) = A\omega^2 T \exp(-b/T), \quad (4)$$

where  $A$  and  $b$  are the intensity and the activation energy of the U-process, respectively. In the case of scattering at dislocations, the relaxation time is assigned as

$$\tau_{\text{dis}}^{-1}(\omega) = D\omega, \quad (5)$$

where  $D$  is parameter dependent on the density of dislocations.

In an isotropic continuum the relaxation rate of the phonons scattered on an isotropic point defects is [24]

$$\tau_R^{-1}(\omega) = C\omega^4, \quad (6)$$

where  $C$  is the Rayleigh scattering parameter,  $C = V_0\Gamma/(4\pi s^3)$ , and  $V_0$  is the volume per molecule. The coefficient  $\Gamma$  determines the intensity of scattering.

The experimental data on  $\kappa(T)$  in phases II and III existing at helium temperature are well described by the calculated curves that allow for the thermally activated, Rayleigh and dislocation mechanisms (see Fig. 6). The fitting parameters for these mechanisms are given in the Table.

Note that below the temperature of the orientation II–III phase transition in pure  $\text{CD}_4$  (and the I–II transition in pure  $\text{CH}_4$ ) the thermal conductivity changes as  $\kappa(T) \propto \exp(b/T)$ . This behavior can be explained assuming that the phonon scattering at librations is a thermally activated process similar to phonon–phonon scattering (U-process) which is of essential importance in high-temperature of phase I. It is obvious that the activation energy  $b$  is more than two times

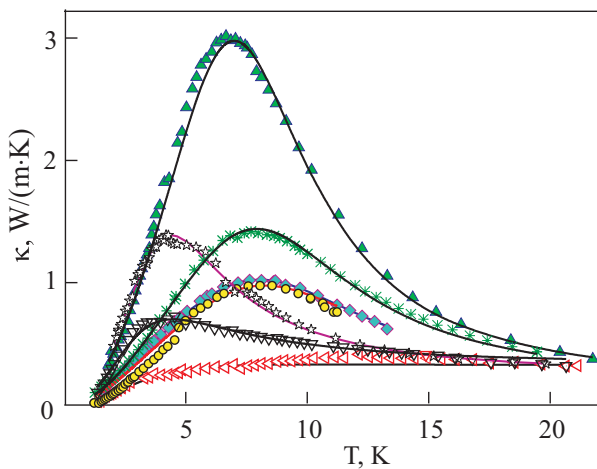


Fig. 6. Thermal conductivity of  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  for  $c = 0$  ( $\star$ ), 0.03 ( $\nabla$ ), 0.06 ( $\triangleleft$ ), 0.22 ( $\circ$ ), 0.40 ( $\blacklozenge$ ), 0.78 ( $\ast$ ), and 1.00 ( $\blacktriangle$ ). Solid lines are calculated curves using fitted parameters from the Table.

Table. Parameters used to describe the thermal conductivity of  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  for the thermoactivated processes ( $\tau_U^{-1}(\omega, T) = A\omega^2 T \exp(-b/T)$ ), scattering at dislocations ( $\tau_{\text{def}}^{-1}(\omega) = D\omega$ ) and Rayleigh scattering ( $\tau_R^{-1}(\omega) = C\omega^4$ )

$c$	$A \cdot 10^{16}$ , s/K	$b$ , K	$D \cdot 10^4$	$C \cdot 10^{12}$ , s <sup>3</sup>
Phase III				
100	35	40	5	7.5
78	35	40	10	35
40	35	40	10	110
22	35	40	12	100
Phase II				
13	9	9	33	30
6	9	9	23	10
3	9	9	6.7	10
0	15	16	4.2	5

higher in pure  $\text{CD}_4$ . There are two main reasons for this difference. First, the barrier hindering reorientations of the molecules is stronger in phase III than in phase II. Second, the moment of inertia of the  $\text{CD}_4$  molecule is twice as large as that of the  $\text{CH}_4$  molecule. In the low-temperature region the character of the dependence  $\kappa(T)$  is determined by phonon scattering at dislocations. Its intensity is almost independent of complete deuteration. The scattering increases in the solution because the density of dislocations becomes higher at the expense of dislocations generated in the process of growing and subsequent cooling the samples. The curve  $\kappa(T)$  measured at the background of dislocation-induced scattering has no signs of resonance scattering at the rotational tunnel states of the molecules. The contribution of the Rayleigh scattering to the thermal conductivity becomes evident in phase III of the concentrated  $(\text{CH}_4)_{1-c}(\text{CD}_4)_c$  solutions. The intensity of the Rayleigh scattering is shown in Fig. 7 as a function of  $\text{CD}_4$  concentration. The parameter  $C$  is nearly an order of magnitude higher than for scattering at isotopic point defects. The difference is due to local changes in the mass of molecules. The parameter  $\Gamma$  describing local mass variations in a molecular crystalline two-component system consisting of two kinds of molecules ( $\text{CH}_4$  and  $\text{CD}_4$ ) with different masses  $M_1$  and  $M_2$  is

$$\Gamma = c(1-c) \left[ \frac{\Delta M}{M} \right]^2, \quad (7)$$

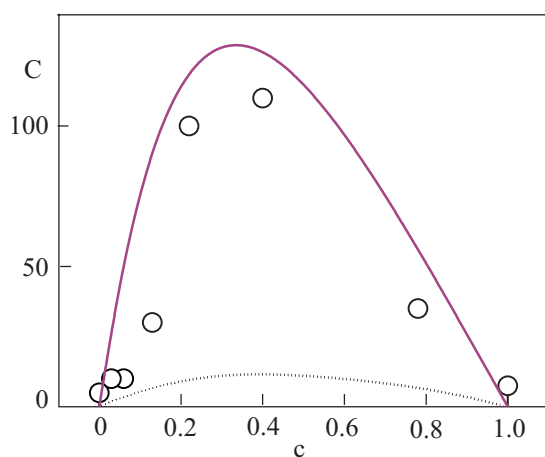


Fig. 7. The Rayleigh scattering parameter  $C$  dependence on CD<sub>4</sub> concentration  $c$  get from: the fitting procedure (○), the calculations using the mass difference of molecules (dotted line) and the difference between the moments of inertia of two molecules (solid line).

where  $\bar{M} = cM_1 + (1-c)M_2$  is the average mass, and  $\Delta M = M_1 - M_2$  is the mass difference.

The above fact suggests an additional mechanism of strong scattering in the orientationally ordered phase of the two-component solution. This is the interaction between the phonons and the librations of molecules. The authors propose a phenomenological description of this mechanism by analogy with the mechanism based on local mass variations.

Diluting CH<sub>4</sub> with CD<sub>4</sub> does not produce a significant change in the picture of tunneling and librational (rotational) states of phase II of solid regular methane. As it has been shown in high-resolution neutron spectroscopy experiments [37], the shift of the lines is less than 10% in the concentration range 0–0.15 of CD<sub>4</sub> molecules in the CH<sub>4</sub>–CD<sub>4</sub> solid solution. The lines are broadened by a factor of ~2–3 in this concentration range. These variations of the energy of the states and the line shapes are not sufficient to explain the dramatic change in the dependence of the thermal conductivity on temperature.

The CD<sub>4</sub> molecule features a stronger effective octupole moment than that of the molecule of CH<sub>4</sub>. Therefore, partial replacement of CH<sub>4</sub> molecules with their heavier isotopic counterpart in the structure of phase II of protonated methane changes (increases) the electrostatic field at the position of the neighbors of the replaced molecules. In particular, it affects the sites of almost freely rotating molecules by lowering the symmetry of the field experienced by the rotating molecule, which in turn results in stronger hindering of the molecule. It means a stronger interaction of the rotating molecule with the surroundings. Therefore, the glassy-like behavior of the thermal conductivity coefficient of the CH<sub>4</sub>–CD<sub>4</sub> crystal can be explained by the enhancement of interaction of the rotations with crystal phonons.

On the other hand, the Rayleigh scattering parameter  $C$  of the molecular crystalline two-component system of two-sorts of molecules (with moments  $I_1$  and  $I_2$ ) is well described by Eq. (7) if the mass of the molecule is replaced by its moment of inertia

$$\Gamma = c(1-c) \left[ \frac{\Delta I}{\bar{I}} \right]^2, \quad (8)$$

where  $\bar{I} = cI_1 + (1-c)I_2$  is the average moment of inertia, and  $\Delta I$  is the difference between the moments of inertia of two molecules.

Equation (8) describes quantitatively with a good accuracy the behavior of the parameter  $C$  in phase III at varying concentration  $c$  (see Fig. 7). Note that a straight forward calculation of thermal conductivity resulting from the phonon-rotational coupling is a complicated and unsolved yet theoretical problem of a three-dimensional lattice. This is a challenge even for a structurally simple orientationally ordered molecular crystal such as (CH<sub>4</sub>)<sub>1-c</sub>(CD<sub>4</sub>)<sub>c</sub>. The influence of local changes in the moments of inertia upon the thermal conductivity points to the importance of kinetic processes for rotational dynamics of orientationally ordered molecules interacting with thermal phonons.

## Conclusions

The thermal conductivity of the solid (CH<sub>4</sub>)<sub>1-c</sub>(CD<sub>4</sub>)<sub>c</sub> with  $c = 0, 0.03, 0.065, 0.13, 0.22, 0.4, 0.78$  and 1.0 has been measured in the region of existence of three orientational phases: disordered (phase I), partially ordered (phase II) and completely ordered (phase III). The temperature interval of measurement was 1.3–30 K. The temperature dependence of the thermal conductivity  $\kappa(T)$  behaves differently in these phases. As the degree of the orientational order increases, the thermal conductivity grows too. In phase I the thermal conductivity is independent of  $c$  and little dependent on  $T$ . The impurity effect in  $\kappa(T)$  is much stronger in the low-temperature region of phase II than of phase III. At increasing  $c$  the curve  $\kappa(T)$  of phase II approaches the dependence typical for phase I. There is a hysteresis in the vicinity of the II↔III phase transition. In phase III the impurity effect in  $\kappa(T)$  can be interpreted as phonon scattering on the rotational defects appearing due to the difference between the moments of inertia of the CH<sub>4</sub> and CD<sub>4</sub> molecules. The hysteresis of the thermal conductivity observed in our experiments indicates that the orientational phase transition from the partially ordered phase to a complete order is a continuous process with an intermediate mixed two-phase stage. The temperature interval of the mixed state increases linearly with the CH<sub>4</sub> concentration in the CD<sub>4</sub> solution. Such continuous transition is possible if the interphase surface energy is low and there are strong temperature

and pressure fluctuations in the presence of defects. The transition is accompanied by the formation of a complex inhomogeneous bulk structure.

The obtained dependences of thermal conductivity on temperature and concentration can be explained qualitatively assuming that the dominant mechanism of phonon scattering is connected with the interaction between the phonons and the rotational motion of the molecules in all of the three orientational phases of the CH<sub>4</sub>-CD<sub>4</sub> system. In the general case this behavior accounts for the lowering degree of the anharmonic rotational motion at increasing orientational order.

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1. A.I. Prokhvatilov and A.P. Isakina, *Fiz. Nizk. Temp.* **10**, 1206 (1984) [*Sov. J. Low Temp. Phys.* **10**, 631 (1984)].
2. F. Lostak, K.O. Prins, and N.J. Trappeniers, *Physica* **B162**, 254 (1990); *Physica* **B162**, 21 (1990); *Physica B+C* **139-140**, 272 (1986).
3. W. Press, *Single-Particle Rotations in Molecular Crystals, Springer Tracts of Modern Physics* 92, Springer, Berlin, Heidelberg, New York (1981).
4. M.A. Neumann, W. Press, C. Noldeke, B. Asmussen, M. Prager, and R.M. Ibberson, *J. Chem. Phys.* **119**, 1586 (2003).
5. A.I. Prokhvatilov and A.P. Isakina, *Phys. State Solidi (a)* **78**, 147 (1983).
6. D. Marx and M. Muser, *J. Phys.: Condens. Matter* **11**, R117 (1999).
7. W. Press, A. Hüller, H. Stiller, W. Stirling, and R. Currat, *Phys. Rev. Lett.* **32**, 1354 (1974).
8. H.M. James and T.A. Keenan, *J. Chem. Phys.* **31**, 12 (1959).
9. W. Press and A. Hüller, *Phys. Rev. Lett.* **30**, 1207 (1973).
10. E. Bartholome, G. Drikos, and A. Eucken, *Z. Phys. Chem.* **39**, 371 (1938).
11. R.G. Ross, P. Andersson, B. Sundqvist, and G. Backstrom, *Rep. Prog. Phys.* **47**, 1347 (1984).
12. L.A. Koloskova, I.N. Krupskii, and V.G. Manzhelii, *J. Low Temp. Phys.* **14**, 403 (1974); V.A. Konstantinov, V.G. Manzhelii, V.P. Revyakin, and S.A. Smirnov, *Physica* **B262**, 421 (1999); G. Manzhelii and I.N. Krupskii, *Fiz. Tverd. Tela* **10**, 284 (1968).
13. A.I. Krivchikov, A.N. Yushchenko, V.G. Manzhelii, O.A. Korolyuk, F.J. Bermejo, R. Fernández-Perea, C. Cabrillo, and M.A. González, *Phys. Rev.* **B74**, 060201(R) (2006).
14. V.A. Konstantinov, *Fiz. Nizk. Temp.* **29**, 567 (2003) [*Low Temp. Phys.* **29**, 422 (2003)].
15. A. Jezowski, H. Misiorek, V.V. Sumarokov, and B.Ya. Gorodilov, *Phys. Rev.* **B55**, 5578 (1997).
16. A.I. Krivchikov, B.Ya. Gorodilov, O.A. Korolyuk, V.G. Manzhelii, and V.V. Dudkin, *Phys. State Solidi (c)* **1**, 2959 (2004).
17. P. Stachowiak, E. Pisarska, A. Jezowski, and A.I. Krivchikov, *Phys. Rev.* **B73**, 134301 (2006).
18. A. Jezowski and P. Stachowiak, *Cryogenics* **32**, 601 (1992).
19. P. Stachowiak, E. Pisarska, A. Jezowski, and A.I. Krivchikov, *Europhys. Lett.* **74**, 96 (2006).
20. A.I. Krivchikov, P. Stachowiak, E. Pisarska, and A. Jezowski, *Phys. Rev.* **B75**, 012303 (2007).
21. B.Ya. Gorodilov, A.I. Krivchikov, and O.A. Korolyuk, *Fiz. Nizk. Temp.* **31**, 1158 (2005) [*J. Low Temp. Phys.* **31**, 884 (2005)].
22. E. Pisarska, P. Stachowiak, and A. Jezowski, *Fiz. Nizk. Temp.* **33**, 768 (2007) [*Low Temp. Phys.* **33**, 587 (2007)].
23. R.M. Kimber and S.J. Rogers, *J. Phys. C: Solid State Phys.* **6**, 2279 (1973).
24. R. Berman, *Thermal Conduction in Solids*, Clarendon Press, Oxford (1976).
25. H. Yasuda, *J. Low Temp. Phys.* **31**, 223 (1978).
26. A. Jezowski, H. Misiorek, V.V. Sumarokov, and B.Ya. Gorodilov, *Phys. Rev.* **B55**, 5578 (1997).
27. O.A. Korolyuk, B.Ya. Gorodilov, A.I. Krivchikov, and V.V. Dudkin, *Fiz. Nizk. Temp.* **26**, 323 (2000) [*Low Temp. Phys.* **26**, 235 (2000)].
28. V.A. Konstantinov, V.G. Manzhelii, R.O. Pohl, and V.P. Revyakin, *Fiz. Nizk. Temp.* **27**, 1159 (2001) [*Low Temp. Phys.* **27**, 858 (2001)].
29. R.M. Lynden-Bell and K.H. Michel, *Rev. Mod. Phys.* **66**, 721 (1994).
30. O.A. Korolyuk, B.Ya. Gorodilov, A.I. Krivchikov, A.S. Pirogov, and V.V. Dudkin, *J. Low Temp. Phys.* **111**, 515 (1998).
31. P. Stachowiak, V.V. Sumarokov, J. Mucha, and A. Jezowski, *Phys. Rev.* **B50**, 543 (1994).
32. P. Stachowiak, V.V. Sumarokov, J. Mucha, and A. Jezowski, *J. Low Temp. Phys.* **111**, 379 (1998).
33. V.V. Sumarokov, P. Stachowiak, J. Mucha, and A. Jezowski, *Phys. Rev.* **B74**, 224302 (2006).
34. P. Stachowiak, V.V. Sumarokov, J. Mucha, and A. Jezowski, *Phys. Rev.* **B67**, 172102 (2003).
35. *Structure and Thermodynamic Properties of Cryocrystals: Handbook*, V.G. Manzhelii (ed.), Begell House Hardcover, Begell House (1998).
36. R.G. Ross, P. Andersson, B. Sundqvist, and G. Backstrom, *Rep. Prog. Phys.* **47**, 1347 (1984).
37. M. Prager and W.J. Press, *Chem. Phys.* **92**, 5517 (1990).