

Heat transfer in different phases of solid cyclohexene



V.A. Konstantinov*, A.I. Krivchikov, O.A. Korolyuk, V.P. Revyakin, V.V. Sagan, G.A. Vdovichenko, A.V. Zvonaryova

B. Verkin Institute for Low Temperature Physics and Engineering, NAS of Ukraine, 47 Lenin Avenue, Kharkov 61103, Ukraine

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ABSTRACT

The thermal conductivity of solid cyclohexene C_6H_{10} has been measured in two independent experiments in five different stable and metastable phase states: orientational glass (Ig), orientational glass (IIIg) with a partial order, dynamically orientational disordered state (III) with a partial order, completely orientational ordered phase (II) and "plastic" phase (I). The measurements were carried out at saturated vapor pressure in the temperature range 2–120 K and at isochoric conditions in "plastic" and orientational ordered phases on samples of different densities. The isochoric thermal conductivity of "plastic" phase increases smoothly with temperature. It can be attributed to weakening of the translational orientational coupling which, in turn, leads to a decrease in phonon scattering on rotational excitations. The thermal conductivity of cyclohexene measured at saturated vapor pressure exhibits a similar behavior in phases Ig, IIIg, and II. At low temperatures ($T < 8$ K) the thermal conductivity tends to T^2 dependence: passes through a maximum and decreases further with increasing temperature following the dependence, which is somewhat different from $1/T$. It was found that the thermal conductivity can be represented as a sum of two contributions $\kappa(T) = \kappa_1(T) + \kappa_2(T)$, where $\kappa_1(T)$ is due to propagating phonons whose mean-free path exceeds half the phonon wavelength, and $\kappa_2(T)$ is attributed to localized short-wavelength or "diffusive" vibrational modes.

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1. Introduction

Recently, much interest has been focused on metastable long-living and stationary solid phases with different types of dynamic and static disorders and on the solid state transformations of a metastable phase to a thermodynamically stable state [1–4]. Some of the molecular crystals possessing the translational symmetry display typical "glassy" properties, in particular, a boson peak [5]. It has been recently shown that the low temperature thermal conductivity of disordered molecular solids is only slightly sensitive to the nature of disorder in them; however, it is extremely sensitive to the kinetics of phase transformations in systems with rotational degrees of freedom [6–10]. This makes the thermal conductivity an efficient tool for the study of orientational defects formed in the course of phase transformations and polymorphous transitions.

For correct comparison with the theory thermal conductivity must be measured on samples having constant densities. This requirement is of particular importance in the region of rather high (premelting) temperatures where the coefficients of thermal expansion of molecular crystals are extremely large. Isochoric and

isobaric data are practically the same at low temperatures where the thermal expansion is small.

Cyclohexene C_6H_{10} is one of few objects suitable to investigate the above properties. It belongs to a limited class of substances consisting of comparatively simple molecules which, however, can develop a wide set of polymorphous states. Many of its properties have been investigated thoroughly, which permits a reliable interpretation of experimental data. The C_6H_{10} molecule is stable when it has a "half-chair" configuration with a double carbon bond. Cyclohexene is also interesting as a representative of organic molecular crystal with monocyclic ring structures that typically exhibit order–disorder phase transitions in the solid state. The existence of a phase transition in this compound has been known for many years [11]. Adiabatic calorimetric studies showed a phase transition at 139 K, with an entropy of transition $\Delta S_f/R = 3.7$ (where R is the gas constant), which is noticeable larger than the entropy of fusion $\Delta S_f/R = 2.3$ at 170 K, indicating the high temperature phase of C_6H_{10} is a "plastic" crystal. A more recent and extensive DTA (the differential thermal analysis) and adiabatic calorimetric studies by Haida and co-workers has shown a more complex phase behavior involving metastable and glassy crystal states, depending on the rate of cooling and the thermal prehistory of the sample [12,13]. It was found that by slow cooling the high temperature "plastic" phase I transforms reversibly to a metastable phase III at 112 K (see Fig. 1). On further cooling below 83 K a

* Corresponding author. Tel.: +380 573410832; fax: +380 573403370.
E-mail address: konstantinov@ilt.kharkov.ua (V.A. Konstantinov).

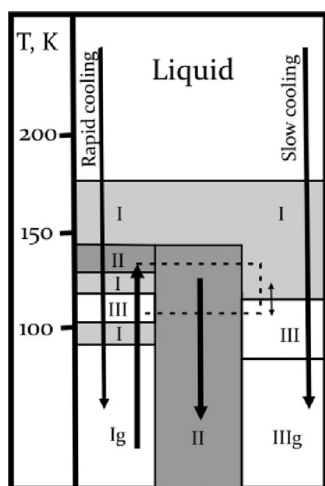


Fig. 1. The diagram of phase transformation in solid cyclohexene for rapid (> 7 K/min) and slow cooling after the work of Haida and co-workers [13].

glassy crystal (phase state IIIg) is formed. Fast cooling (> 7 K/min) can quench the sample into a glass-like state of phase I (orientational glass Ig), which when heated undergoes a series of overlapping transitions some of which are exothermic; $Ig \rightarrow I \rightarrow III \rightarrow I \rightarrow II \rightarrow I \rightarrow \text{liquid}$ at 81 K, 100 K, 115 K, 120 K, 140 K, and 170 K, respectively. The stable low temperature phase II develops reversibly from phase I on annealing to $T = 120$ K. It can be then cooled down to the low temperatures. The temperature of $I \rightarrow II$ phase transition depends both on the thermal prehistory of the sample and on its purity. This unusual sequence of phase transitions was explained by Haida and co-workers using a Gibbs free energy schematic diagram. Thus, cyclohexene has two glassy orientationally disordered crystalline phases (orientational glass Ig and orientational glass IIIg with a partial order), and completely ordered low temperature phase II. The transitions between phases I, II and III are first-order phase transitions, whereas the $I-Ig$ and $III-IIIg$ transitions are actually processes of “freezing” of the rotational disorder in the crystal. Such kind of polymorphism demonstrating the existence of both ordered and disordered molecules in a crystal lattice can be observed, for example, in CD_4 and solid CH_4-CD_4 solutions and in some simple organic substances, which can have different phases with the complete orientational order, a partial orientational order and the complete orientational disorder [8,9].

The structures of the above phases were investigated on single-crystal samples using a X-ray technique and high-resolution powder neutron diffraction [14]. Phase I is cubic with space group $Pa3$ and has eight molecules per unit cell, which are incorporated into a “herringbone” type structure. Phase II is the completely orientationally ordered, crystallizing in the triclinic space group $P1$ with two molecules per unit cell: chains of the molecules are arranged one above another along the vector perpendicular to the basal plane. Metastable phase III is monoclinic with space group $P2_1/c$ with eight molecules per unit cell and exhibits a pseudo cubic character inherited from the phase I structure. In this phase III, four molecules are orientationally ordered and other four molecules in the unit are dynamically disordered and exhibits ring inversion which freezes below the glass transition temperature $T_g = 83$ K.

The orientational motion of the molecules and the behavior of the phase transitions in cyclohexene were also investigated by spectroscopic methods. The temperature dependences of the second NMR moment and the spin–lattice relaxation time are in good agreement with the calorimetric data taken on a fast-cooled sample [15]. Phase I of cyclohexene has a dynamical orientational

disorder which corresponds to a free one-axis rotation of molecules and to the inversion relative to the molecular ring plane, whereas metastable phase III corresponds only to the inversion. This complex phase behavior was also observed in Raman and IR spectroscopic investigations [16]. The spectra of stable phase II differ from those of all other phases and are consistent with those of the monoclinic or triclinic crystalline structures (C_{2h} or C_i) having two molecules in the unit cell. In contrast, phase I is characterized by asymmetric lines and smeared maxima in the low-frequency region of the Raman spectra which are indicative of an anisotropic rotation of the molecules. The frequency of the ring-inversion mode is significantly different in different phases.

2. Experimental results

The thermal conductivity of solid cyclohexene C_6H_{10} has been measured in two independent experiments in different stable and metastable phases. The measurements were carried out at saturated vapor pressure in the temperature range 2–120 K and at isochoric conditions in “plastic” and orientationally ordered phases on samples of different density at temperatures from 85 K up to the melting. The purity of cyclohexene (Sigma-Aldrich) was up to 99.0%. The isochoric thermal conductivity was measured by a steady-state method using a coaxial setup. The pressure of samples growing was varied within 40–130 MPa at the temperature gradient about 1.5 K/cm along the measuring cell. When the sample growth was completed, the inlet capillary was blocked by freezing it with liquid nitrogen. The total systematic error of measurement was up to $\pm 4\%$. For more experimental details see Ref. [17].

The isochoric thermal conductivity of cyclohexene measured on different density samples is shown in Fig. 2. Sample N1 was grown under pressure of 60 MPa. After cooling to $T = 150$ K (corresponding to orientationally disordered “plastic” phase I) the inlet capillary was blocked, the sample was annealed for 3 h and then cooled slowly (~ 2.0 K/min) down to $T = 115$ K to remain in phase I (see the right-hand part of the diagram in Fig. 1). The isochoric thermal conductivity was measured during heating of the sample. It increased smoothly with temperature rising up to the onset of melting at $T_m = 185$ K (at constant density of the sample T_m shifts toward higher temperatures). Such temperature

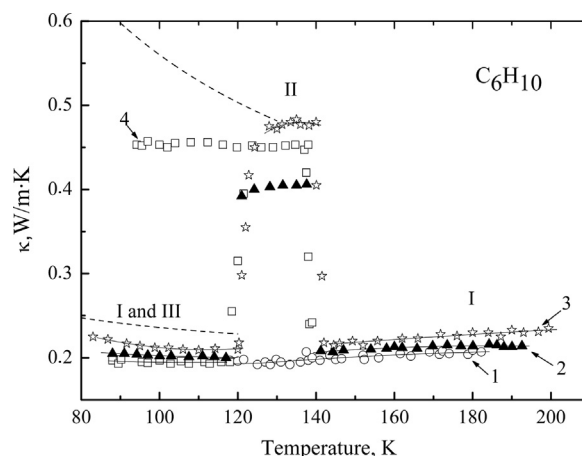


Fig. 2. The isochoric thermal conductivity of cyclohexene measured on different-density samples: N1 (“rings”, $V_m = 134.7$ cm³/mole), N2 (“triangles”, $V_m = 133.2$ cm³/mole), N3 (“stars”, $V_m = 132.1$ cm³/mole), and N4 (“squares”, $V_m = 134.5$ cm³/mole). The lower dashed lines shows the dependence of $\kappa(T) = 4.6/T + 0.19$ for orientational glass Ig and the upper one shows $\kappa(T) = 34/T + 0.22$ for completely orientationally ordered phase II of cyclohexene measured under equilibrium vapor pressure (see Figs. 5 and 6).

dependence of thermal conductivity is fairly typical for “plastic” phases of molecular crystals and can be attributed to weakening of translational orientational coupling which, in turn, leads to a decrease of phonon scattering at the rotational excitations of molecules [18]. Samples N2–4 were prepared on fast cooling (> 8 K/min) down to the temperature of the liquid nitrogen (see the left-hand part of the diagram in Fig. 1). The thermal conductivity measured at the subsequent heating up to 120 K exhibited no appreciable features related to the expected $I_g \rightarrow I \rightarrow III \rightarrow I$ phase transitions. This may be because the nature of orientational disorder (static or dynamic) has little effect on the thermal conductivity. It should also be noted that the density of cyclohexene changes slightly at the $I \leftrightarrow III$ transformation ($\sim 0.7\%$), whereas it changes almost by 4% at $I \leftrightarrow II$ phase transition [14], so our measurements of phase II were actually made under the saturated vapor pressure. The magnitude of the thermal conductivity in orientationally ordered phase II is 2–2.5 times higher than those of phase I and III, and it is strongly dependent on the sample prehistory. Sample N4 was heated into the orientationally ordered phase, annealed for 1.5–2 h at $T = 135$ K and then cooled slowly (~ 0.2 K/min) down to $T = 90$ K to remain in phase II (see the central part of the diagram in Fig. 1). The thermal conductivity was measured during heating of the sample. Its magnitude is in good agreement with the data measured under the saturated vapor pressure. The dashed lines in Fig. 2 show the dependences of $\kappa(T)$ for orientational glass I_g and for completely orientationally ordered phase II of cyclohexene measured under equilibrium vapor pressure (see Figs. 5 and 6). However, the temperature dependence of the thermal conductivity in isobaric and isochoric experiments in phase II has a different slope. This may be due to a possible detachment of the sample from the cell walls in isochoric experiment owing to 4% change of density at $I \leftrightarrow II$ phase transition. The Bridgman coefficient $g = -(\partial \ln \kappa / \partial \ln V)_T$ calculated from our experimental data is 6.2 ± 0.5 in orientationally disordered “plastic” phase I.

The low temperature studies of thermal conductivity of cyclohexene in different phase states were carried out under equilibrium vapor pressure using the experimental setup based upon the steady-state method (the setup and the technique are detailed in Ref. [19]). The liquid cyclohexene was put into the container of the measuring cell blowing with helium. The loaded cell was then placed in the cryostat chamber and cooled down to 2 K with a cooling rate of 7.8 K/min to obtain the phase I_g , and the thermal conductivity was measured in this state at $2 \text{ K} < T < T_g$. Then sample was heated up to 135 K and annealed to obtain the phase II; during annealing some heat release was observed. After preparation of phase II, its thermal conductivity was measured in the temperature interval 2–120 K. To make sure that cooling rate was sufficient to obtain state I_g , sample was melted at 220 K and then cooled down to 60 K with rate of 15.5 K/min and the thermal conductivity was measured once again at $2 \text{ K} < T < T_g$. In both cases, the thermal conductivity of the samples coincided. Phase III was prepared from the phase I at annealing of the sample at temperature about 103 K, and after that the sample was cooled slowly down to 2 K to obtain the phase state III_g . The thermal conductivity was measured in state III_g at $2 \text{ K} < T \leq T_g$. At heating some heat release was observed at $T_g = 83$ K caused by $III_g \rightarrow III$ transformation, and then the thermal conductivity was measured in state III at $T_g < T \leq 110$ K.

The thermal conductivity of cyclohexene measured in the phase states I– I_g , II, III– III_g under equilibrium vapor pressure is shown in Fig. 3. It is seen that all three curves have similar dependences. At low temperatures ($T < 8$ K) the thermal conductivity tends to T^2 dependence. As the temperature increases the thermal conductivity passes through maximums at 15 K, 25 K and 13 K in the phases I_g , II and III_g respectively. Above 40 K the

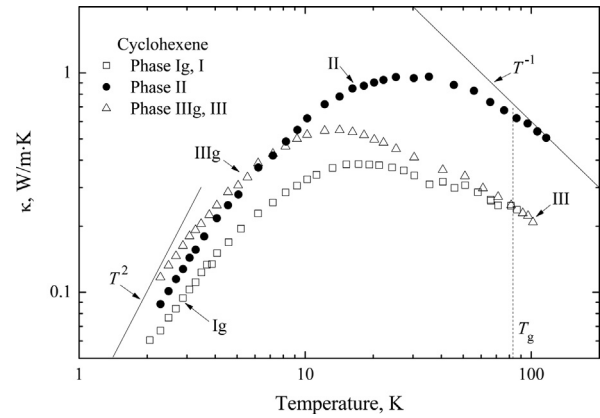


Fig. 3. The temperature dependence of the thermal conductivity of solid cyclohexene at low temperatures in different phase states: I– I_g , II and III– III_g , measured under equilibrium vapor pressure using the experimental setup based upon the steady-state method. $T_g = 81$ K and 83 K is the glass transition temperature for I_g and III_g , respectively. The solid lines indicate the temperature dependences $\kappa(T) \propto T^2$ and $\kappa(T) \propto T^{-1}$.

thermal conductivity decreases following the dependence which is somewhat different from $1/T$. The thermal conductivity of phase II is appreciably higher than those of phase states I_g , III_g and III at $T > 10$ K. However, below this temperature the thermal conductivity of phase II is lower than that of phase state III_g , and it is steeper than in phase states I_g and III_g . The heat in this temperature region is transferred predominantly by phonons having large mean-free path and their scattering mechanisms (scattering by dislocations and point defects) strongly dependent on quality of the crystal. Since phase II was obtained by annealing of phase I at $T = 135$ K and its subsequent fast cooling, the resulting crystal might contain numerous defects dislocations, point defects etc.

3. Discussion

The rotational degrees of freedom of the molecules in phase states I and III are frozen below the temperatures of glass formation. State I_g is an orientational glass. Half of the molecules in state III_g is orientationally ordered, while the other half is orientationally disordered. State I_g has much in common with the orientational glass in ethanol [6]. The thermal conductivity of phase III has a kink near $T_g = 83$ K (see Fig. 3). The heat capacity also has a singularity at this temperature, which is evidence in favor of the $III \rightarrow III_g$ transition [12]. The similar kink is also observed in phase I near the glass transition temperature T_g . The kink is more prominent in Fig. 4 which shows the thermal conductivity of phases I– I_g and III– III_g in the coordinates $\kappa(T) \times T$.

In general case the thermal conductivity of dielectric crystals can be presented as sum of two contributions [7,18,20–29]:

$$\kappa(T) = \kappa_1(T) + \kappa_2(T). \quad (1)$$

The contribution $\kappa_1(T)$ is due to propagating phonons whose mean-free path is larger than the phonon half-wavelength. The contribution $\kappa_2(T)$ is attributed to localized or “diffuse” short-wavelength vibrational modes. Above 40 K the thermal conductivity of cyclohexene can be approximated with a good accuracy by the expression $\kappa(T) = A/T + B$, where the term A/T describes the three-phonon Umklapp processes and the term B presents the additional mechanism of heat transfer that operates in the high-temperature region. At present there is no established theory including both the mechanism of heat transfer. However, it is experimentally found that at sufficiently high temperatures B can be taken as a constant [22]. The coefficients A and B in this study

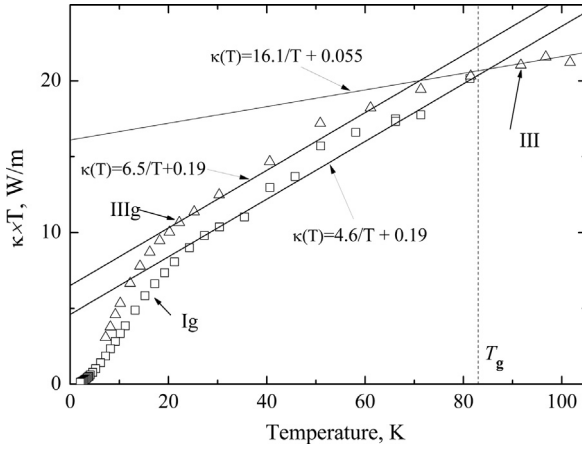


Fig. 4. The temperature dependence of the thermal conductivity of solid cyclohexene in the coordinates $\kappa(T) \times T$ for phases Ig, I and IIIg, III. Labels are the same as in Fig. 3. Straight lines are approximation of experimental results by the expression $\kappa(T) = A/T + B$, coefficients A and B are shown in Table 1.

Table 1

Coefficients A and B , the number of atom per unit cell (Z), and structures of phases Ig, II, IIIg, and III of cyclohexene.

Phase	Ig	II	IIIg	III
A , W/m	4.6 ± 0.1	34 ± 0.1	6.5 ± 0.1	16.1 ± 0.1
B , W/m K	0.19	0.22	0.19	0.055
Z	8	2	8	8
Structure	Cubic Pa3	Triclinic P1	Monoclinic P2 ₁ /c	Monoclinic P2 ₁ /c

were obtained by a linear approximation of the thermal conductivity curves in coordinates $\kappa(T) \times T$. They are listed in the Table 1 along with the number of atoms per unit cell (Z) and the structure of corresponding phases.

It is seen that the parameter A that depends on the intensity of phonon–phonon scattering has the highest value in ordered state (the lowest intensity of phonon scattering). The parameter B is only weakly dependent on structure.

To analyze the results obtained, the thermal conductivity was split into two components $\kappa_1(T)$ and $\kappa_2(T)$. Coefficient κ_2 was calculated within the framework of Cahill–Pohl model [20] so that at high temperatures $\kappa_2(T)$ is equal to the coefficient B :

$$\kappa_2 = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \nu \left(\frac{T}{\theta}\right)^2 \int_0^{\theta/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \quad (2)$$

where ν is the sound velocity, θ is the Debye temperature ($\theta = v\hbar/k_B$) ($(6\pi^2 n)^{1/3}$), n is the number of molecules per unit volume, $x = \hbar\omega/k_B T$.

The contribution of $\kappa_2(T)$ to the thermal conductivity is rather small at low temperatures but it increases with temperature and becomes a determining factor at high temperatures. $\kappa_2(T)$ was calculated using the ν and θ values of Table 2. The density of cyclohexene was taken from Ref. [14] and the sound velocity was measured at ILTPE NASU by G.A. Zviagina and K.R. Zhekov.

The phonon contribution κ_1 was calculated as a difference between the experimental thermal conductivity and κ_2 . The selected phonon $\kappa_1(T)$ and “diffusive” $\kappa_2(T)$ components of the thermal conductivity in phases I, II and III are shown in Figs. 5–7.

It is seen that at low temperatures the phonon component κ_1 varies approximately as T^2 , passes through a maximum at rising

Table 2

B_U and E_U are the coefficient of the phonon scattering and the characteristic energy of the U -processes respectively, D_d and D_p are the coefficients of phonon scattering at dislocations and by point defects, respectively, ν is the sound velocity, ρ is the density, and θ is the Debye temperature.

Phase	I	II	III
B_U , 10^{-16} s/K	1.46	1.58	9.35
E_U , K	254	275	211
D_d , 10^{-3}	3.44	2.9	1.9
D_p , 10^{-40} s ³	5.12	1.33	3.42
ν , m/s	1600	1660	1640
ρ , kg/m ³	1120	1214	1185
θ , K	96.2	102.5	100.5

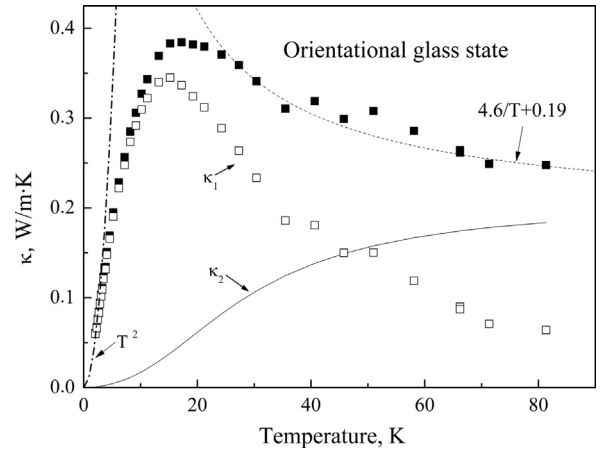


Fig. 5. The contribution of phonons and “diffusive” modes to the thermal conductivity of orientational glass state Ig of cyclohexene. Symbols: ■ are experimental data, □ is κ_1 contribution, and solid line is κ_2 contribution. The dashed line indicates the dependence of $\kappa(T) = A/T + B$ (see the coefficients A and B in Table 1). The dash-dot line indicated the dependence of $\kappa(T) \sim T^2$.

temperature, and then decreases. At high temperatures $\kappa_1(T)$ follows the dependence which is somewhat different from $1/T$. The calculated κ_1 was compared with that obtained in the Debye–Peierls time-relaxation model:

$$\kappa_1 = \frac{k_B}{2\pi^2 \nu} \left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta/T} \frac{\tau x^4 e^x}{(e^x - 1)^2} dx \quad (3)$$

where the relaxation time τ is determined by the U -processes (τ_U^{-1}), phonon scattering by dislocations (τ_d^{-1}) and scattering by point defects (τ_p^{-1}):

$$\tau_U^{-1}(\omega, T) = B_U \omega^2 T e^{-E_U/T} \quad (4a)$$

$$\tau_d^{-1}(\omega, T) = D_d \omega \quad (4b)$$

$$\tau_p^{-1}(\omega, T) = D_p \omega^4 \quad (4c)$$

here B_U and E_U are the coefficient and the characteristic energy of U -processes respectively, D_d is the coefficient of scattering at dislocations, and D_p is the coefficient of scattering at point defects.

The temperature dependences of the phonon component $\kappa_1(T)$ calculated in the framework of Debye–Peierls model for the above three phase states considering the U -processes and the phonon scattering by dislocations and point defects are shown in Fig. 8. It is seen that the calculated curves describe the phonon component $\kappa_1(T)$ quite adequately in the whole temperature range.

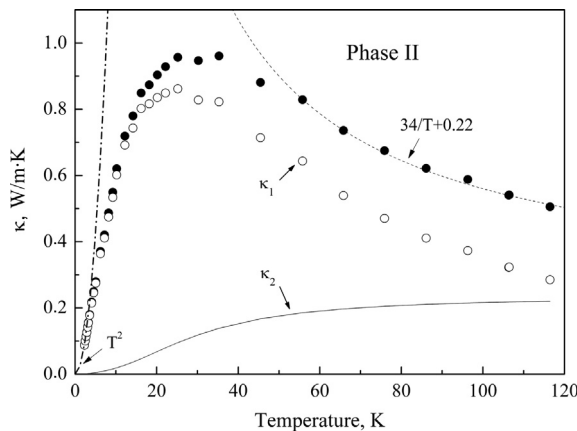


Fig. 6. The contributions of phonons and “diffuse” modes to the thermal conductivity of orientationally ordered phase II of cyclohexene. Symbols: • are experimental data, ○ κ_1 contribution, and solid line is κ_2 contribution. The dashed line indicated the dependence of $\kappa(T) = A/T + B$ (see the coefficients A and B in Table 1). The dash-dot line indicated the dependence of $\kappa(T) = T^2$.

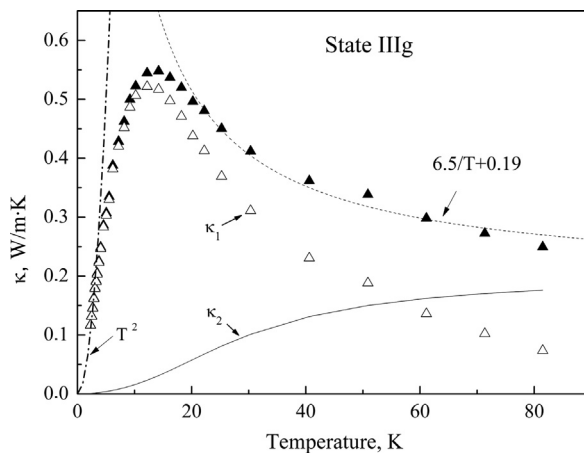


Fig. 7. The contributions of phonons and “diffuse” modes to the thermal conductivity of partly orientationally ordered glass state IIIg of cyclohexene. Symbols: ▲ are experimental data, △ κ_1 contribution, and solid line is κ_2 contribution. The dashed line indicated the dependence of $\kappa(T) = A/T + B$ (see the coefficients A and B in Table 1). The dash-dot line indicated on the dependence of $\kappa(T) = T^2$.

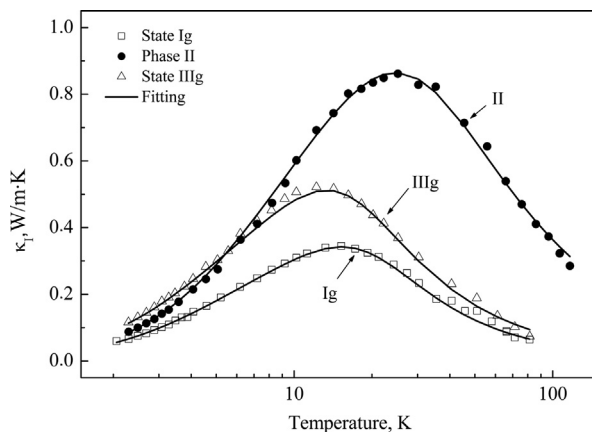


Fig. 8. The phonon part of the temperature dependence of thermal conductivity $\kappa_1(T)$ of cyclohexene in different phase states. The solid line is the approximation of the experimental results within the time-relaxation model.

The phonon scattering coefficients B_U , D_d , D_p , the characteristic energy of the U -processes E_U , the sound velocity v , the density ρ and Debye temperature θ are given in Table 2.

4. Conclusion

The thermal conductivity of solid cyclohexene C_6H_{10} has been measured in two independent experiments in five different stable and metastable phase states: I, Ig, II, III and IIIg. The measurements were carried out at saturated vapor pressure in the temperature range 2–120 K and at isochoric conditions in “plastic” and orientationally ordered phases on samples of different density at temperatures from 85 K up to the melting. The isochoric thermal conductivity of orientationally disordered “plastic” phase I increases smoothly with temperature. This behavior is fairly typical for “plastic” phases of molecular crystals and can be attributed to weakening of translational orientational coupling which, in turn, leads to a decrease of phonon scattering at the rotational excitations of molecules. The magnitude of the thermal conductivity in orientationally ordered phase II is 2–2.5 times higher than those of phase I and III and is strongly dependent on the sample prehistory.

The thermal conductivity of cyclohexene measured under saturated vapor pressure has the same features in different crystal states: orientational glass (Ig), orientational glass (IIIg) with a partial order, dynamically orientationally disordered state (III) with a partial order and completely orientationally ordered phase (II). At low temperatures ($T < 8$ K) the thermal conductivity tends to T^2 dependence. As temperature increases the thermal conductivity passes through maximums at 15 K, 25 K and 13 K in the phases Ig, II and IIIg, respectively. Above 40 K thermal conductivity decreases with temperature by the law which is somewhat different from $1/T$. The thermal conductivity of phase II is appreciably higher than those of phases Ig and IIIg above 10 K. In all the phases the thermal conductivity of cyclohexene can be represented as a sum of two contributions $\kappa(T) = \kappa_1(T) + \kappa_2(T)$, where $\kappa_1(T)$ is due to propagating phonons whose mean-free path exceeds half the phonon wavelength, and $\kappa_2(T)$ is attributed to localized short-wavelength or “diffusive” vibrational modes. It is shown that the phonon component can be described adequately in all the cases within the framework of Debye–Peierls model taking into account the U -processes and the phonon scattering at dislocations and point defects.

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