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THERMAL CONDUCTIVITY OF MOLECULAR CRYSTALS WITH SELF-ORGANIZING DISORDER

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The thermal conductivity of some orientational glasses of protonated C_2H_5OH and deuterated C_2D_5OD ethanol, cyclic substances (cyclohexanol $C_6H_{11}OH$, cyanocyclohexane $C_6H_{11}CN$, cyclohexene C_6H_{10}), and freon 112 ($CFCl_2)_2$ have been analyzed in the temperature interval 2–130 K. The investigated substances demonstrate new effects concerned with the physics of disordered systems. Universal temperature dependences of the thermal conductivity of molecular orientational glasses have been revealed. At low temperatures, the thermal conductivity exhibits a universal behavior that can be described by the soft potential model. At relatively high temperatures, the thermal conductivity has a smeared maximum and than decreases with increase in the temperature, which occurs typically in crystalline structures.

K e y w o r d s: thermal conductivity, orientational glass, phonon scattering, soft potential model.

1. Introduction

Orientational glasses form a relatively small class of crystalline molecular materials, in which the centers of molecular masses reside at the lattice sites and their orientations and/or conformations are disordered. According to the position of the centers of molecular masses, these substances are crystals; on the other hand, they are glasses possessing specific properties. Of special interest are the temperature dependences of the thermal conductivity $\kappa(T)$ of these objects. They deviate from the corresponding dependences typical of orientationally-ordered molecular crystals: there is no phonon maximum in most of them [1–3]. The dependences $\kappa(T)$ also differ from those typically observed in structural glasses; they have no plateau and do not increase with a rising temperature [4].

It was demonstrated with protonated ethanol [1] that the thermal conductivity curves of orientational and structural glasses having basically different molecular disorderings were unexpectedly close in value and temperature dependence. This finding was then confirmed in the investigation of the thermal conductivity of deuterated ethanol [2]. The behavior of the thermal conductivity of ethanol glasses suggests that the acoustic phonon scattering in glasses is caused mainly by the orientational molecular disor-

der rather than the structural one. This stimulated a search for common regularities in the dependence $\kappa(T)$ of orientational glasses.

2. Materials

Solid alcohols are suitable objects to investigate the low-temperature anomalies and the thermal properties of disordered systems [5]. By selecting the thermal prehistory of samples, these molecular H-bonded solids can be transformed easily into a different solid state with a structural or orientational disorder. In the homologous series of monoatomic alcohols, only ethanol (protonated or deuterated) can exist in the state of orientational glass. This state is obtainable in both protonated and deuterated ethanols at the cooling below $T_g = 97$ K. The obtained glass has a bcc structure. The investigation of the thermal conductivity of the orientational glasses of monoatomic alcohols was logically continued on cyclic alcohols – cyclohexanol $C_6H_{11}OH$ and its analogs: cyanocyclohexanol $C_6H_{11}CN$, cyclohexene C_6H_{10}, and freon 112 $(CFCl_2)_2$.

In this class of substances, the state of orientational glass evolves due to the orientational disorder which occurs, when the rotational motion of the molecules in a plastic crystal is frozen, and the molecule can vary its conformation in a flexible carbon skeleton.

The cyclohexanol molecule is a ring formed by a cyclic carbon radical with a functional hydroxyl group

-OH fixed on it. Structural and calorimetric investigations show that the pseudospheric form and the functional group enable the molecule to change into different conformations and to exhibit an interesting polymorphic behavior [6–10]. At low temperatures, the substance can exist in several solid phases depending on the thermodynamic prehistory of the sample.

Phase I is a stable orientationally disordered state, in which the molecules rotate almost freely at the sites of the fcc lattice. Phase I develops due to the crystallization of a liquid at the cooling below the melting temperature $T_m = 299$ K. Note that phase I is supercooled readly at moderate cooling rates and transforms into an orientational glass at $T_g = 148$–150 K [9, 11].

Phase II having a tetragonal structure (space group $P\bar{4}2_1c$ [8]) can be obtained either at the smooth cooling of phase I below $T = 265.5$ K or at the heating of metastable ordered phase III to $T = 220$–240 K.

Phase III (space group Pc) can be obtained by heating an orientational glass above the glass formation temperature at $T \approx 200$ K. According to recent results [8], the cyclohexanol ring takes a "chair" conformation in all ordered phases.

According to recent findings, there are two factors responsible for the disorder in the orientational glass of molecular cyclic structures such as cyclohexanol and the related substances. These are a mixture of conformations and a disordered orientation of the molecule as a whole [6].

Cyanocyclohexane $C_6H_{11}CN$ is also rich in polymorphism due to the presence of various conformers. In addition to the ring conformations determined by the position of the cyanic group with respect to the ring, the cyanocyclohexane molecule has axial and equatorial conformations. According to IR and Raman data [12], the latter conformations can interconvert at energies $\sim E/k_B = 4500$ K. They have identical occupancies in phase I and in the liquid state; low-temperature orientationally ordered phase II has only an axial conformation [12].

Orientationally disordered fcc phase I of cyanocyclohexane evolves due to the crystallization of the liquid ($T_m = 285$ K). The glassy state is formed at the cooling of phase I at $T_g \sim 135$ K (see calorimetric and dielectric spectroscopy data [13, 14]). A small jump of the heat capacity was also observed near 55 K [15], which was attributed to the frozen interconversion of the axial and equatorial conformers. At the heating

above 271 K, phase I transforms into stable orientationally ordered phase II. The conclusion about the state of phase II of cyanocyclohexane is based only on the measurement of enthalpy variations during the II-I phase transition [15]. No structural evidence is available to support it.

Of all the discussed substances, cyclohexene possesses the widest range of polymorphism. It can be obtained in five solid states depending on the temperature prehistory of the sample. Owing to the double bond in the carbon ring, the "half-chair" conformation is the most stable form of the molecule.

Cooling below the crystallization temperature transforms a liquid sample into a plastic crystal (phase I) having the fcc structure and a dynamic orientational and conformational disorder. At the fast cooling below $T_g = 81$ K, the plastic crystal changes into an orientational glass.

Annealing at $T = 120$–140 K transforms phase I into stable completely ordered low temperature phase II. The molecules of phase II are orientationally ordered.

At the slow cooling below 112 K, phase I transforms into metastable phase III, in which half the molecules are orientationally ordered, and the others have dynamic orientational and conformational disorder. At the further cooling below 83 K, the motion of the disordered molecules is frozen, and a state, in which only half the molecules are orientationally ordered, is formed. Metastable phase III is monoclinic with eight molecules per unit cell. It exhibits a pseudocubic behavior inherited from the structure of phase I.

Freon 112 $(CFCl_2)_2$ is the final substance in the investigated series of orientational glasses. Its molecule is not cyclic and has no hydrogen bonds. The orientational glass state evolves, because the molecules can exist in two molecular conformations – *gauche* and *trans*. The change into an orientational glass occurs at the cooling of a high-temperature orientationally disordered bcc phase slightly below $T_g = 90$ K. There is information in the literature [16, 17] that freon 112 is the most fragile substance among the known orientational glasses.

3. Results and Discussion

The thermal conductivities of some orientation glasses (protonated and deuterated ethyl alcohols, cyclohexanol, cyanocyclohexane, cyclohexene, and

freon 112) have been analyzed. The goal was to search for regularities in the behavior of the temperature dependence of the thermal conductivity at low temperatures. The thermal conductivity of these substances was measured previously [1–4, 18] in the interval from 2 K to the glass transition temperature, by using the steady-state method [19, 20].

The temperature dependences of the thermal conductivity of the orientational glasses of protonated C_2H_5OH and deuterated C_2H_5OD ethanol [1, 2] are illustrated in Fig. 1.

The curves $\kappa(T)$ have three distinct temperature intervals, in which the thermal conductivity exhibits different behavior: a low temperature region below 5 K, an interval of 5–50 K, and high temperature region above 50 K. At low temperatures ($T < 5$ K), the thermal conductivity grows most rapidly. In the interval 5–50 K, it forms a smeared "plateau," and its growth is weaker than in the region $T < 5$ K. In these intervals, the behavior of the thermal conductivity can be described as $\kappa = \alpha \cdot T^n$, the exponent n and the coefficient α are close for both the substances in each interval (see Table 1).

At $T = 50$ K, the thermal conductivity of the orientational glass of deuterated ethanol is about 1.3 times higher than that of protonated ethanol. The difference can be explained qualitatively on the grounds of heat transfer: in this temperature interval, the hopping heat transfer can start operating in addition to the "diffuse" heat transfer. Both of the mechanisms are sensitive to the density of the vibrational states of phonons.

As the temperature increases ($T > 50$ K), the thermal conductivity of the orientational glass of the protonated alcohol (unlike the deuterated one) is saturated. The thermal conductivity of the orientational glass of the deuterated alcohol has a smeared maximum in a vicinity of 50 K. At the further rise of the temperature, its dependence can be described as $A/T + C$. This suggests that, in the high-temperature region, where the orientational glass of deuterated alcohol is influenced by the "diffusive" and hopping mechanisms of heat transfer, it also experiences the processes of phonon-phonon scattering. Such processes are typical in orientationally ordered crystals at temperatures above the phonon maximum of thermal conductivity.

This behavior of the thermal conductivity in the state of orientational glass is at variance with what
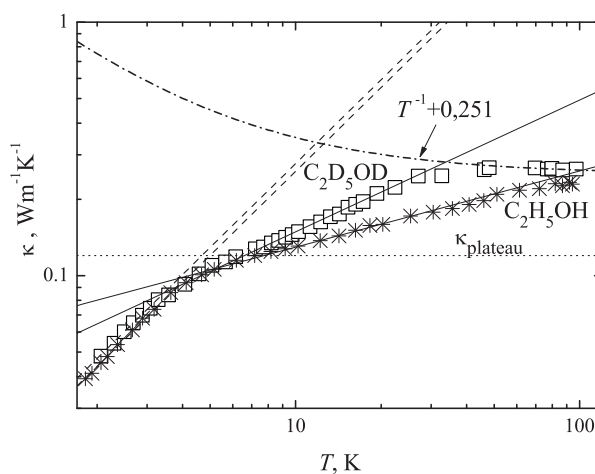

Fig. 1. Temperature dependence of the thermal conductivity of orientational glasses of protonated (∗) and deuterated (□) ethanol [2]. The solid and dashed straight lines show the power law of the thermal conductivity $\kappa = \alpha \cdot T^n$; the dotted line is the thermal conductivity at the beginning of the "plateau" $\kappa_{plateau}$; the dash-dotted line is the dependence $\kappa(T) = A/T + C$, where $A = 1$ Wm^{-1}, $C = 0.251$ Wm^{-1}K^{-1}

is observed in structural glasses, in which the thermal conductivity continues to grow monotonically, as the temperature increases above the interval of the "plateau."

The thermal conductivities of the orientational glasses of cyclohexanol [4], cyanocyclohexane [3], and cyclohexene [18] are shown in Fig. 2. The curves $\kappa(T)$ of cyclohexanol and cyanocyclohexane behave much like $\kappa(T)$ of deuterated ethanol: they have similar three regions. The only difference is that the smeared maximum of the thermal conductivity is shifted to 30 K. It is seen that, at $T < 5$ K and in the smeared "plateau" region, where the phonon heat transfer is operative, the thermal conductivity behaves like that of a structural glass. The thermal conductivities of cyanocyclohexane and cyclohexene follow the power law $\kappa = \alpha \cdot T^n$ like that of ethanol (see Table 1).

In the smeared "plateau" region, the powers n for cyclohexanol and cyanocyclohexane ($n = 0.54$) differ significantly from n measured for glycerol ($n = 1$) [21], in which the dependence $\kappa(T)$ is linear above the "plateau" temperature. The difference owes to the rotational degrees of freedom of the orientational glass molecules that influence the dependence $\kappa(T)$ in these cyclic substances.

The rotational degrees of freedom may also affect the dependence $\kappa(T)$ in the orientational glass of the
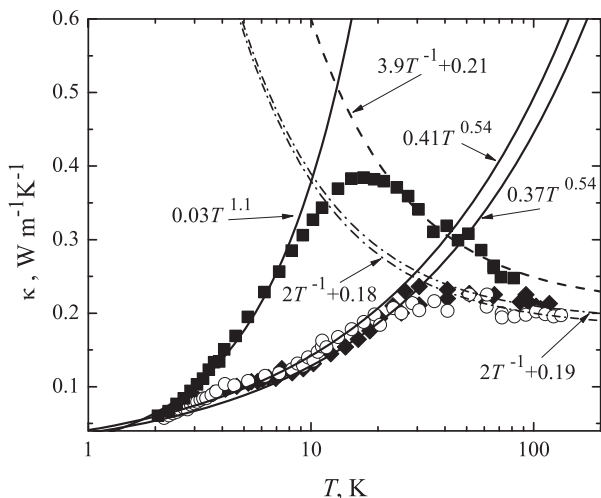
Fig. 2. Thermal conductivities of the orientational glasses of cyanocyclohexane (○) [3], cyclohexanol (♦) [4], and cyclohexene (■) [18]. The solid lines show the power law of the thermal conductivity $\kappa = \alpha \cdot T^n$. The dashed and dash-dotted lines are the dependence $\kappa(T) = A/T + C$

cyclohexene, in which its behavior more closely resembles that in orientationally ordered crystals.

At low temperatures, the dependence of $\kappa(T)$ follows the law $\kappa = \alpha \cdot T^n$, but the power n is higher than those for the other cyclic substances. The thermal conductivity reaches its peak at $T = 17$ K and then drops, as in orientationally ordered crystals. Note that, in the orientational glass of cyclohexene, the dependence $\kappa(T)$ is similar to that of a completely ordered crystal, the difference being merely quantitative.

Table 1. **Basic parameters of the power law $\kappa = \alpha \cdot T^n$ describing the thermal conductivity of the orientational glasses in two temperature intervals $T < 5$ K and 5–50 K. A and C are the coefficients of the dependence $\kappa(T) = A/T + C$, observed at $T > 50$ K**

Samples	$T < 5$ K		5–50 K		$T > 50$ K	
	$\alpha, \frac{Wm^{-1}}{K^{n+1}}$	n	$\alpha, \frac{Wm^{-1}}{K^{n+1}}$	n	$A, \frac{W}{m}$	$C, \frac{W}{m \cdot K}$
C_2H_5OH	0.020	1.1	0.065	0.3	–	–
C_2D_5OD	0.022	1.1	0.045	0.52	1	0.251
$C_6H_{11}OH$	0.026	1	0.037	0.54	2	0.19
$C_6H_{11}CN$	0.026	1	0.041	0.54	2	0.18
C_6H_{10}	0.030	1.1	–	–	3.9	0.21
$(CFCl_2)_2$	0.065	0.8	0.1	0.12	9.5	0

Since the cyclohexene molecule is pseudospherical and has no hydrogen bonds, its orientational disorder provides no strong scattering, like the other investigated orientational glasses. In the whole temperature region of the orientational glass of cyclohexene, the temperature dependence of the thermal conductivity resembles that of an orientationally ordered crystal with numerous defects.

At high temperatures, the thermal conductivities of the three cyclic substances demonstrate the great importance of the phonon-phonon scattering. For example, above 30–40 K, the thermal conductivity of these substances can be described by the dependence $\kappa(T) = A/T + C$ (see Fig. 2 and Table 1).

The temperature dependence of the thermal conductivity coefficient of freon 112 (Fig. 3) has similar three temperature regions, which can be described by the dependences found for ethanol, cyclohexanol, and cyanocyclohexane. The parameters are given in Table 1. Of all the considered orientational glasses, that of freon 112 has the most extended plateau (from 5 K to 50 K) and the lowest exponent n. The plateau is between two maxima of the thermal conductivity. The low-temperature maximum is at $T = 4.5$ K, and another one (a smeared maximum) is at $T = 50$ K. The behavior of the temperature dependence of the thermal conductivity changes abruptly, when the temperature rises above 50 K. At $T > 60$ K, the thermal conductivity of freon 112 is described by the dependence typical of orienatationally ordered crystals; $\kappa(T) = A/T + C$, $C = 0$. This behavior suggests a profound effect of the phonon-phonon scattering, which is manifested in the coefficient A accounting for the intensity of the phonon-phonon processes (see Table 1).

The coefficient A varies from 0 for protonated ethanol to 9.5 for freon 112. The high value of A in freon 112 may be attributed to the exceptional fragility of its orientational glass, which distinguishes it among the investigated orientational glasses [16, 17]. The coefficient A tends to increase with the molar mass of orientational glass. The tendency correlates with the behavior of the coefficient A in the orientationally ordered phases of simple alcohols, in which it increases almost linearly with the molar mass [22].

Thus, the thermal conductivity of the investigated orientational glasses reveals a specific temperature behavior: it is glass-like in the temperature region, where the heat is transferred by phonons, and is

crystal-like at high temperatures, where the phonon-phonon scattering comes into play in addition to the "diffusive" and hopping mechanisms of heat transfer.

The experimental results on the thermal conductivity of the investigated orientational glasses were analyzed in terms of the relaxation time, which was described within the soft-potential model. In this model, the inverse phonon mean free path can be subdivided into three components describing the processes of resonance scattering of acoustic phonons at anharmonic defects. The defects involve tunnel states, classical relaxation processes, and quasilocalized low-frequency harmonic vibrations. These processes differ only in energy. Their intensities are determined by the dimensionless parameter $\bar{C}$, which characterizes the binding force between the acoustic phonons and the two-level systems and is generalized to all quasilocal excitations within the soft-potential model. The energy W is another important parameter in this model. W is the characteristic energy describing practically all soft modes.

According to the soft-potential model, the reduced thermal conductivity $\kappa(T)\bar{C}v/W^2$ (v is the sound velocity) as a function of the reduced temperature should be independent either of the structure or the chemical composition of the substance, at least at low temperatures up to the plateau region. To compare the theoretical and experimental results, we calculated the thermal conductivity as a function of the temperature within the soft-potential model using the universal expression [23]

$$\kappa(T) = \frac{W^2}{\bar{C}v}F(z),$$

where $z = k_\mathrm{B}T/W$ is the dimensionless variable (normalized temperature), and the function $F(z)$ is

$$F(z) = \frac{z^2 k_\mathrm{B}}{2\pi^2\hbar^2}\int\limits_0^\infty \Big(\frac{1}{1.1tanh(x/2) + 0.7z^{3/4} + x^3z^3/8} \times$$

$$\times \frac{x^3 e^x}{(1-e^x)^2}\Big)dx.$$

The function $F(z)$ depends only on the normalized temperature (z).

The dependence of the reduced thermal conductivity on the reduced temperature that was obtained from the experimental results measured on the orientational glasses of protonated and deuterated ethyl
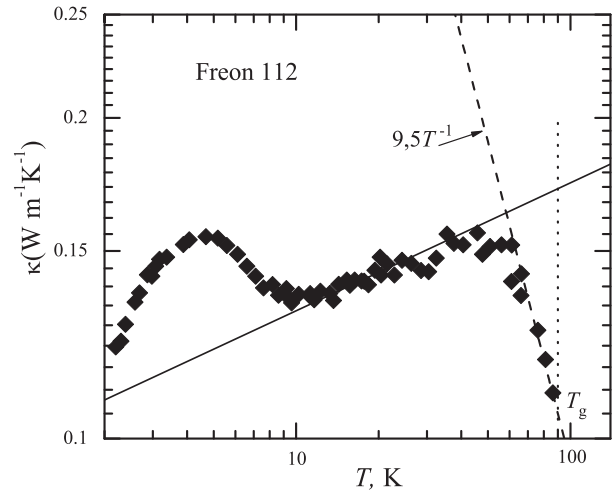

Fig. 3. Thermal conductivity of freon 112 in the orientational glass state [3]. The solid straight line is the power law $\kappa = \alpha \cdot T^n$ describing the behavior of the thermal conductivity. The dotted line shows the glass formation temperature $T_g = 90$ K
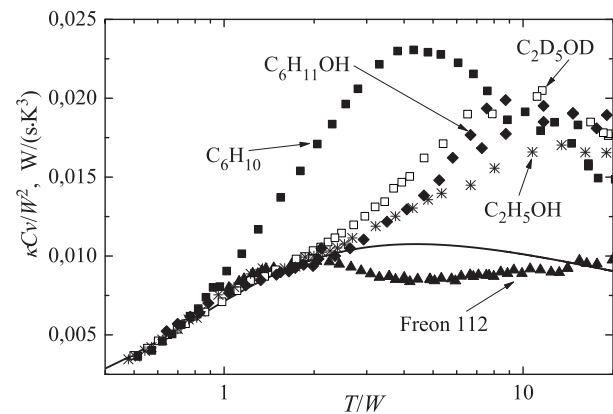

Fig. 4. Reduced thermal conductivity $\kappa(T)\bar{C}v/W^2$ as a function of the reduced temperature T/W. The symbols mark the experimental data on the thermal conductivity of the orientational glasses of cyclohexanol [4], cyclohexene [18], protonated and deuterated ethanol [2], and freon 112 [3]. The solid line is the universal dependence based on the soft potential model

alcohols, cyclohexene, cyclohexanol, and freon 112 is illustrated in Fig. 4. The solid line is the unified universal curve based on the soft potential model. It is seen that, at low temperatures $T < 7.2$ K, the experimental thermal conductivities of all orientational glasses can be described by a single universal curve obtained within the soft potential model.

Table 2. **Parameters W and $\bar{C}$ of the soft potential model obtained by fitting the theoretical curve to the experimental results taken on the orientational glasses**

Samples	m, g/mol	W, K	$\bar{C}$, 10^{-4}	T_g, K
C_2H_5OH	46.07	3.8	8.2	97
C_2D_5OD	52.11	4.1	9.0	97
$C_6H_{11}OH$	100.16	3.5	4.6	148–150
$C_6H_{11}CN$	109.16	3.5	4.8	135
$(CFCl_2)_2$	203.8	2.3	2.8	90
C_6H_{10}	82.14	4	6	81

The exception is cyclohexene, in which this temperature interval is smaller, $T < 3.3$ K. The experimental data depart from the universal curve only in the high temperature region $T/W > 2$, where the weak phonon scattering changes to the strong one (Ioffe–Regel crossover). The parameters of the soft potential model were estimated by fitting the universal dependence of the function $F(z)$ to the experimental results for the thermal conductivity of orientational glasses. The parameters are available in Table 2.

In the low-temperature region, the theoretical curve based on the soft potential model describes well the experimental results measured on the orientational glasses of the substances consisting of the linear and cyclic molecules. It also describes adequately the temperature behavior of the thermal conductivity in the orientation glasses of substances with or without hydrogen bonds.

In the high temperature region, when the "diffusive" and hopping mechanisms are in operation, the orientational glasses also experience the effect of the phonon-phonon scattering typical of orientationally ordered crystals above the temperature of the phonon maximum of the thermal conductivity.

4. Conclusion

The temperature dependences of the thermal conductivity of the orientational glasses of protonated and deuterated ethanol, cyclic cyclohexanol alcohol (including its analogs – cyanocyclohexane and cyclohexene), and freon 112 have been analyzed. Universal temperature dependences of the thermal conductivity have been revealed in the investigated orientational glasses. At low temperatures, the thermal conductivity exhibits a universal behavior that can be described by the soft potential model. At high temper-

atures, the thermal conductivity has a smeared maximum and then decreases with increase in the temperature, following the law $\kappa(T) = A/T + C$, which is common to crystalline structures and is caused by the phonon-phonon scattering.

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ТЕПЛОПРОВІДНІСТЬ
МОЛЕКУЛЯРНИХ КРИСТАЛІВ З БЕЗЛАДДЯМ,
ЩО САМООРГАНІЗУЄТЬСЯ

Р е з ю м е

Проведено аналіз теплопровідності деяких орієнтаційних стекол – протонованого C_2H_5OH і дейтерованого C_2D_5OD етанолу та циклічних сполук – циклогексанолу $C_6H_{11}OH$, цианоциклогексану $C_6H_{11}CN$, циклогексену C_6H_{10}, а також фреону 112 $(CFCl_2)_2$ в температурному інтервалі 2–130 К. Ці речовини демонструють нові ефекти, що відносяться до фізики розупорядкованих систем. Виявлено універсальні залежності теплопровідності молекулярних орієнтаційних стекол: при низьких температурах спостерігається універсальна поведінка теплопровідності, що описується моделлю м'яких потенціалів; при відносно високих температурах спостережено розмитий максимум теплопровідності та її зменшення з подальшим зростанням температури, що характерно для кристалічних структур.