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HEAT TRANSFER IN PLASTIC PHASES OF CYCLIC HYDROCARBONS

V. Konstantinov, V. Sagan, V. Revyakin,
A. Karachtvtseva

*B. Verkin Institute for Low Temperature Physics and Engineering
47 Lenin Ave., 61103 Kharkov, Ukraine
e-mail: konstantinov@ilt.kharkov.ua*

Thermal conductivity of «plastic» phases of furan (C_4H_4O) and cyclopentane (C_5H_{10}) has been measured at isochoric conditions for samples of different densities. It increases with temperature in furan and phase I of cyclopentane and is nearly constant in phase II of cyclopentane. Such behavior is attributed to weakening of the translational orientational coupling which, in turn, leads to a decrease of phonon scattering on rotational excitations. A comparison has been made with the behavior of the thermal conductivity of previously studied benzene (C_6H_6) and cyclohexane (C_6H_{12}).

Key words: thermal conductivity, «plastic» phases, furan, cyclopentane.

Many properties of molecular crystals are closely related to the character of the rotational motion of the molecules in the crystal lattice sites. In general case it can pass through the following stages depending on the relation between central and noncentral forces and temperature: growth of the libration amplitudes, appearance of jump-like reorientations of molecules, increase of the frequency of reorientations, hindered rotation of the molecules and, finally, nearly free rotation of the molecules. The latter type of the molecular motion is extremely rare in its pure form, and it is realized, apparently, only in hydrogen and methane. The existence of crystals with a number of interesting properties, including low entropy of fusion, was first detected by Timmermans, who called them “plastic crystals” [1]. As a convenient criterion of belonging to the plastic crystal Timmermans considered the low entropy of fusion: $\Delta S_f \leq 2.5 R$; (where R is the gas constant). Plastic crystals are formed, as a rule, by globular molecules, i.e. molecules with high symmetry. A specific example of an orientationally disordered phase is a rotation of the molecules around a chosen axis or rotation of molecular fragments. The influence of such kind of molecular motion on thermal conductivity is comparatively little studied. For cyclic compounds such investigations was performed previously only for benzene C_6H_6 [2] and cyclohexane C_6H_{12} [3].

For correct comparison with the theory at $T \geq \Theta_D$ (Θ_D is the Debye temperature) thermal conductivity must be measured at constant density to exclude the thermal expansion effect. Here we present study of the isochoric thermal conductivity in «plastic» phases of solid furan (C_4H_4O) and cyclopentane (C_5H_{10}).

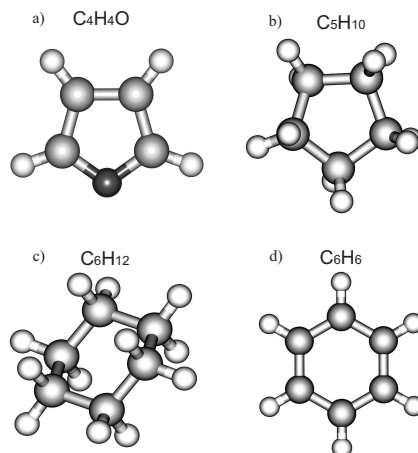


Рис. 1: The shapes of hydrocarbon molecules investigated: a) furan, b) cyclopentane, c) cyclohexane, d) benzene.

Furan (C_4H_4O) molecule is a planar five-membered heterocycle with one oxygen atom (see Fig. 1a). Solid furan has a phase transition at 150 K with an entropy of transition $\Delta S_{I-II}/R=1.6$ and melts at 187.6 K with entropy of fusion $\Delta S_f/R=2.3$ indicating that the high temperature phase of furan can be attributed to the plastic crystal [4]. As follows from X-ray diffraction data phases I and II have orthorhombic ($Cmca$, $Z=4$ molecules per cell) and tetragonal ($P_{41}2_12$ or $P_{43}2_12$, $Z=4$) structures correspondingly [5]. Phase I is disordered with molecules randomly distributed among four equivalent coplanar orientations. NMR studies reveal a sharp change of the line width at the II \rightarrow I transition from 4.95 G² to 1.42 G² (G - gauss), which is close to the theoretical estimates for the rigid lattice and for the rotator phase [6]. The NMR data have shown that the disorder is dynamic, and that the molecules reorient rapidly among the four allowed orientations. Previously, the thermal conductivity of furan was investigated at constant pressures in the temperature range of 113-274 K [7].

Cyclopentane (C_5H_{10}) is a cycloaliphatic organic molecule consisting of the ring of five carbon atoms with two hydrogen atoms above and below the plane of carbon skeleton (see Fig. 1b). Molecule can exist in two essentially isoenergetic puckered-ring conformations: half-chair C_2 and bent C_S that are in dynamic equilibrium and interconvert by an isoenergetic process called pseudorotation [8]. Cyclopentane has two phase transitions at 122.4 K and at 138.1 K with entropy of transitions $\Delta S_{III}/R=4.8$ and $\Delta S_{I\rightarrow II}/R=0.3$ respectively, and melts at 179.7 K with entropy of fusion $\Delta S_f/R=0.4$ implies that the phases I and II of cyclopentane are plastic crystals and that they are only slightly more ordered than the liquid state [9].

The structure of solid cyclopentane was studied using method X-ray single-crystal, X-ray powder and neutron powder diffraction [10]. Phase I has a hexagonal space group with $Z = 2$. Phase III has a monoclinic unit cell P_1/c with $Z = 1$. The neutron powder pattern from phase II showed a significant background contribution indicative of a disordered plastic crystal with a large unit cell, or maybe incommensurate, however, the exact

structure has not been determined.

A solid-state NMR study of the disordered phase II has interpreted the rotational motion of molecules in this phase being characterized by pseudorotations around 5-fold molecular axis in conjunction with librational freedom [11]. The study has also indicated the molecular dynamics in phase I as nearly isotropic. On the other hand, MMD (molecular dynamic) simulations of the plastic phases of cyclopentane have highlighted the presence of some correlations between the pseudorotational motion of the molecule around its center of mass and the internal puckering motion of the ring [12].

We also give below some information about previously investigated cyclohexane and benzene. In contrast to benzene (whose molecules have a flat ring shape, see Fig. 1d), the atoms forming the cyclohexane molecule do not lie in one plane: a «chair» conformer is predominant at temperatures below room temperature (see Fig. 1c). Solid cyclohexane (C_6H_{12}) undergoes a phase transition at 186.1 K with a large change in the entropy ($\Delta S_{I-II}/R=4.33$) and melts at 279.8 K with a low entropy of melting ($\Delta S_f/R=1.14$) implies that phase I is the plastic crystal [13]. As follows from X-ray diffraction data plastic phase of cyclohexane has an fcc structure $Fm\bar{3}m$ with $Z=4$ [14]. Phase II has a monoclinic structure with space group $C2/c$ and $Z=4$. Upon heating from 155 to 180 K the second moment of NMR in the low temperature phase decreases sharply from 26 to 6 G², which indicates the appearance of a contribution from a jumplike change in the molecule orientation with respect to the threefold axis [15]. The polymorphic transformation is accompanied by a continuous change in the second moment and the relaxation time. Therefore, it was concluded that molecules in high-temperature phase I have a significant degree of orientational freedom, so that the intermolecular contribution to the second moment becomes negligibly small.

Solid benzene (C_6H_6) exists only in one orthorhombic crystallographic modification $Pbca$ with $Z=4$ [16]. Benzene melts at 278.5 K with the entropy of fusion $\Delta S_f/R=4.2$ [17], which is noticeably larger than the Timmermanns criterion for plastic phases. However, in the crystalline benzene molecules can easily repositioned in the ring plane between the six possible orientations. These six positions are indistinguishable from each other, so there is no thermodynamic transition associated with this reorientation [18].

Isochoric measurements were carried out on a device with coaxial geometry using a stationary method. The measurement technique is described in details in Ref. [19]. The purity of cyclopentane and furan was higher than 99%. The measurement error was $\pm 4\%$. The isochoric thermal conductivity of furan and cyclopentane for the most dense samples with the molar volumes of 58.75 cm³/mole and 74.5 cm³/mole respectively, are shown in Fig. 2 along with the data for earlier studied cyclohexane ($V_m=95.0$ cm³/mole) [3] and benzene ($V_m=70.5$ cm³/mole) [2]. It is seen that in all plastic cyclic hydrocarbons the thermal conductivity increases with increasing temperature except for the phase II of cyclopentane, where it is approximately constant and benzene. In benzene $\kappa_V(T)$ decreases firstly with increasing temperature, passes through a minimum at $T=220$ K, and then increases weakly up to melting. Recall that the nature of the rotational motion of molecules in the substances presented is quite different. In the furan molecules reorient rapidly among the four allowed coplanar orientations. In the benzene molecules can easily repositioned in the ring plane between the six possible orientations.

In the cyclopentane the rotational motion of molecules in phase II being characterized by pseudorotations around 5-fold molecular axis in conjunction with librational freedom,

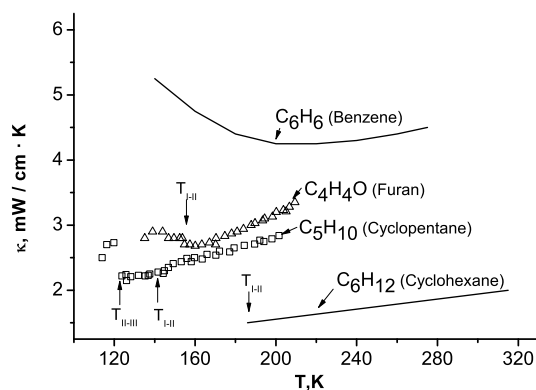


Рис. 2: Isochoric thermal conductivity in the «plastic» phases of cyclic hydrocarbons: furan, cyclopentane, cyclohexane and benzene.

whereas the molecular dynamics in phase I is nearly isotropic. In the «plastic» phase of cyclohexane molecules in high-temperature phase I have a significant degree of orientational freedom, close to their motion in the fluid phase.

The increase of thermal conductivity with temperature can be attributed to a weakening of the translation orientation coupling when the rotational motion of molecules around the ring axis becomes less hindered. The total thermal resistance of the orientationally disordered phases in molecular crystals is a sum of phonon-phonon and phonon-rotation components, $W_{tot} = W_{ph-ph} + W_{ph-rot}$. The phonon-phonon component of the total thermal resistance always increases with temperature, and the phonon-rotation component is comparable (in absolute value) with the phonon-phonon component in ordered phases and tends toward zero when passing to free rotation of molecules. W_{tot} decreases (respectively, the thermal conductivity $\kappa = 1/W$ increases) if W_{ph-rot} decreases faster than W_{ph-ph} increases. For the first time the growth of the thermal conductivity with temperature was observed in the methane and an appropriate explanation of the observed effect was suggested [20]. Thus, we can conclude that disinhibition of uniaxial rotation of the molecules in the cyclic hydrocarbons leads to the increases of the thermal conductivity with temperature like plastic phases of other molecular crystals [21].

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ТЕПЛОПРОВІДНІСТЬ В ПЛАСТИЧНИХ ФАЗАХ ЦИКЛІЧНИХ ВУГЛЕВОДНІВ

В. Константинов, В. Саган, В. Рєвякін, А. Карачевцева

*Фізико-технічний інститут низьких температур ім. Б.І.
Веркіна Національної академії наук України
проспект Леніна, 47, 61103, Харків, Україна
e-mail: konstantinov@ilt.kharkov.ua*

Теплопровідність «пластичних» фаз фурану (C_4H_4O) та циклопентану (C_5H_{10}) була виміряна в ізохоричних умовах для зразків різної щільності. Було виявлено, що вона зростає з температурою в фурані та в фазі I циклопентану, а також, близька до константи в фазі II (C_5H_{10}). Така поведінка пояснюється послабленням трансляційно-орієнтаційної взаємодії, що призводить до послаблення фонового розсіювання на обертових збудженнях. Проводиться порівняння з поведінкою теплопровідності раніше досліджених бензену (C_6H_6) та циклогексану (C_6H_{12}).

Ключові слова: теплопровідність, «пластичні» фази, фуран, циклопентан

**ТЕПЛОПРОВОДНОСТЬ В ПЛАСТИЧЕСКИХ ФАЗАХ
ЦИКЛИЧЕСКИХ УГЛЕВОДОРОДОВ****В. Константинов, В. Саган, В. Ревякин, А. Карачевцева**

*Физико-технический институт низких температур им. Б.И.
Веркина Национальной академии наук Украины
проспект Ленина, 47, 61103, Харьков, Украина
e-mail: konstantinov@ilt.kharkov.ua*

Теплопроводность «пластических» фаз фурана (C_4H_4O) и циклопентана (C_5H_{10}) была измерена в изохорных условиях для образцов различной плотности. Было установлено, что она возрастает при увеличении температуры в фуране и в фазе II циклопентана, а также, близка к константе в фазе II (C_5H_{10}). Такое поведение объясняется ослаблением трансляционно-ориентационного взаимодействия, что приводит к уменьшению фононного рассеивания на вращательных возбуждениях. Проводится сравнение с поведением теплопроводности, исследованных ранее, бензола (C_6H_6) и циклогексана (C_6H_{12}).

Ключевые слова: теплопроводность, «пластические» фазы, фуран, циклопентан