

Isochoric thermal conductivity of solid furan

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Thermal conductivity of solid furan has been measured at isochoric conditions in the high-temperature orientationally-disordered phase I for samples of different densities. Our isochoric data show a gradual increase of Λ_V with temperature whereas isobaric thermal conductivity goes down in this temperature range. The above effect is most clearly expressed in furan, where the atoms in the ring plane are not equivalent, as compared with earlier studied C_6H_6 and C_6H_{12} . The increase of Λ_V with temperature can be attributed to weakening of the translational-orientational interaction which, in turn, leads to a decrease of phonon scattering on rotational excitations. The experimental data are described in terms of a modified Debye model of thermal conductivity with allowance for heat transfer by both low-frequency phonons and “diffuse” modes.

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Introduction

The thermal and mechanical properties of molecular crystals are essentially determined by the character of the rotational motion of the molecules. With increasing temperature the rotational motion can in principle pass through the following stages: 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. Studies of the isochoric thermal conductivity of simple molecular crystals established general relationships in the heat transfer that result from the presence of rotational degrees of freedom at temperatures of the order of the Debye temperature and above $T \geq \Theta_D$ [1]. A strong translational-orientational (TO) interactions contribute significantly to the thermal resistance $W = 1/\Lambda$. This, in turn, leads to large deviations of the isochoric thermal conductivity from the $\Lambda \propto 1/T$ law owing to its approach to a certain lower limit Λ_{\min} . The concept of the lower limit of the thermal conductivity comes from the idea that Λ_{\min} is reached when the heat transfer occurs as diffusion of thermal energy between neighboring quantum-mechanical oscillators, the life time of which is assumed close to one-

half the period of the oscillations [2]. During the transition to weakly hindered rotation in “plastic” phases of molecular crystals, the TO contribution to the total thermal resistance decreases sharply, so that the isochoric thermal conductivity $\Lambda_V(T)$ increases with increasing temperature [1].

A more specific example of an orientationally-disordered phase is rotation of the molecules around a chosen axis or rotation of fragments of molecules. The influence of this kind of motion on the thermal conductivity is comparatively little studied. For cyclic compounds such studies have been performed previously only for benzene C_6H_6 [3] and cyclohexane C_6H_{12} [4]. For a correct comparison with theory at $T \geq \Theta_D$, thermal conductivity must be measured at constant density to exclude the thermal expansion effect. It was found that $\Lambda_V(T)$ of benzene decreases with increasing temperature, passes through a minimum at $T \approx 220$ K, and then increases weakly up to melting. This behavior was attributed to a weakening of the translation–orientation interaction when the rotational motion of benzene molecules around the ring axis becomes less hindered. The isochoric thermal conductivity of solid cyclohexane decreases with increasing temperature in orientationally ordered phase II, and increases in orientationally disordered phase I.

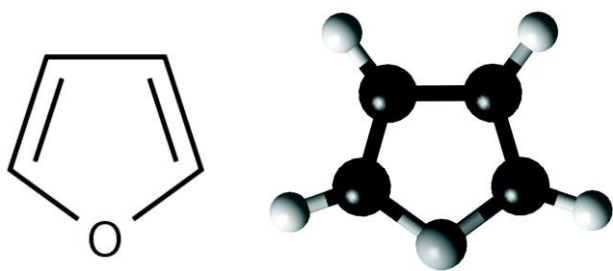


Fig. 1. Furan molecule.

The purpose of this work is to continue the study of the heat transfer peculiarities in simple cyclic hydrocarbons for example of solid furan C_4H_4O . Furan molecule is a five-membered heterocycle with one oxygen atom (see Fig. 1). If the aromatic character of benzene is due to complete symmetry of the molecule and the coplanarity of the bonds, despite the fact that the furan molecule is planar, the atoms in the cycle are not identical, and therefore the bonds are not aligned. According to calorimetric data furan undergoes a phase transition at 150 K and melts at 187.55 K at saturated vapor pressure [5]. A relatively low entropy jump on melting ($\Delta S_m/R = 2.44$, where R is the gas constant) implies that phase I of furan is a plastic crystal. As follows from x-ray diffraction data it has orthorhombic structure (space group $Cmca$) with four molecules per unit cell [6]. Furthermore, this phase is disordered with molecules randomly distributed among four equivalent coplanar orientations. The disorder of phase I is also confirmed by Raman measurements in the lattice mode region [7]. NMR studies reveal a sharp change of the line width at the $II \rightarrow I$ transition from 4.95 to 1.42 Gs^2 , whereas the theoretical estimates give 5.12 Gs^2 for the rigid lattice case and 1.45 Gs^2 for the rotator phase [8,9]. The results of NMR and dielectric [10] studies have shown that the disorder is dynamic, and that the molecules reorient rapidly among the four allowed orientations.

The first order transition to phase II at 150 K is isothermal, with a relatively small entropy jump ($\Delta S_m/R = 1.64$). Phase II has the tetragonal structure (space group $P4_12_12$ or $P4_32_12$) with four oriented molecules per unit cell [6]. The structure is ordered in the sense that each molecule has a unique allowed orientation. The thermal measurements of Guthrie *et al.* [5] also showed a small lambda point at ~ 56 K, thus possibly indicating the existence of a phase III below this temperature. Previously, the thermal conductivity of furan was investigated at constant pressures of 0.11 and 1.2 GPa in the temperature range of 113–274 K [11].

Results and discussion

Here we present the study of the isochoric thermal conductivity of solid furan C_4H_4O in orientationally-disordered orthorhombic phase I on samples of different densities. Isochoric measurements were carried out on a device

with coaxial geometry using a stationary method. The samples were grown under different pressures (20, 60 and 110 MPa for samples N1, N2 and N3, respectively), the temperature gradient along the measuring cell being about 2.5 K/cm. As the growth was completed, the inlet capillary was blocked by cooling it with liquid nitrogen and the samples were annealed for 3–4 h to remove density gradients. The sample characteristics are given in Table 1 and Fig. 1. The measurement technique is described in detail in Ref. 12. Furan of 99.8% purity was used. The measurement error was $\pm 4\%$.

Table 1. Molar volumes V_m of samples, temperatures T_0 of the beginning of meeting the condition $V = \text{const}$ in an experiment, and the temperature T_m of the onset of melting of a sample

Sample No.	$V_m, \text{cm}^3/\text{mole}$	T_0, K	T_m, K
1	60.6	174	198
2	59.9	165	205
3	58.75	150	220

To visualize the characteristics of the measured samples the V - T phase diagram is desirable. Although such data for furan are lacking, a schematic phase diagram can be constructed on the basis of x-ray data from [6], P - V - T data from [13] and the present study. It is shown in Fig. 2. The left-hand lines reflect the change in volume of furan with temperature at saturated vapor pressure with corresponding jumps at $I \leftrightarrow II$ transition and melting. The right-hand curves reflect $I \leftrightarrow II$ transition lines and melting lines. The dashed lines show molar volumes of samples studied. In samples of moderate densities the pressure drops to zero at a certain characteristic temperature T_0 and the isochoric condition is then broken; on further cooling, the sample can separate from the walls of the cell. In the case of a fixed volume, melting occurs in a certain temperature interval and its onset T_m shifts towards higher temperatures with increasing density.

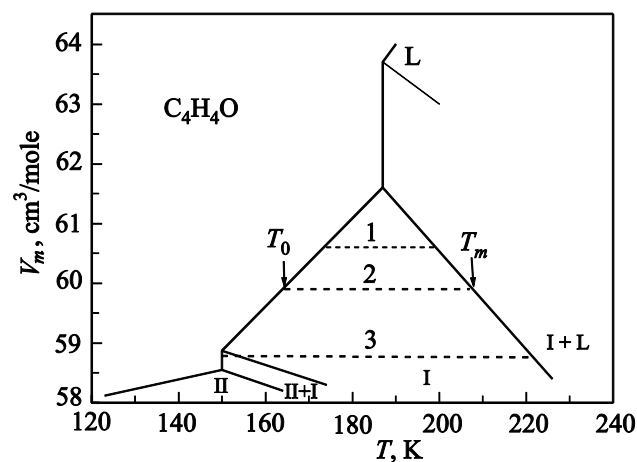


Fig. 2. Schematic V - T phase diagram of furan. The dashed lines show the molar volumes of the samples studied.

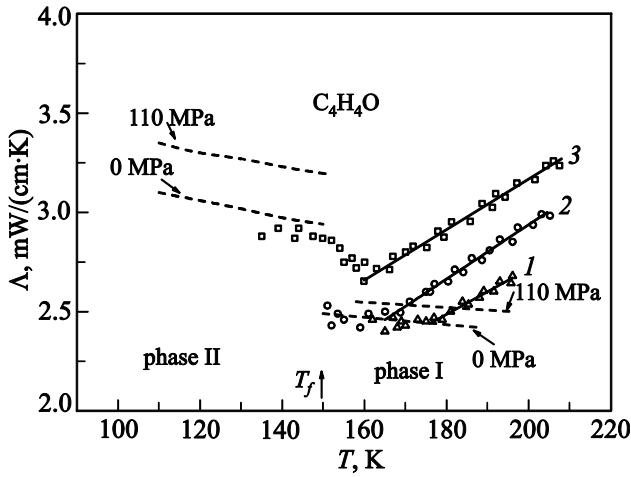


Fig. 3. The isochoric thermal conductivity of three solid furan samples of different densities: $V_m = 60.6$ (N1), 59.9 (N2), 58.75 (N3) cm^3/mole . The solid lines show the smoothed values of the thermal conductivity. The data measured at constant pressure from [11] are shown by dashed lines.

The isochoric thermal conductivity of furan is shown in Fig. 3 along with the data measured at constant pressure [11]. The latter are shown as dashed lines. Thermal conductivity values corresponding to zero pressure were recalculated using data on the known pressure dependence of the thermal conductivity [11]. Isochoric thermal conductivities of all three samples increases with temperature in phase I. Below the temperature T_0 , the pressure in the cell drops to zero, and there is a kink in the thermal conductivity curve. For the most dense sample 3 there is a break with the subsequent increase in conductivity with decreasing temperature below T_0 , associated with the phase transition $I \leftrightarrow II$ (the arrow pointing up with T_f next to it indicate the phase transition temperature $I \leftrightarrow II$ at zero pressure). Our results agree well with the data in [11] reduced to zero pressure except for the values below 140 K for sample 3, where the sample might peel off from the walls. The Bridgman coefficient $g = -(\partial \ln \Lambda / \partial \ln V)_T$ calculated from our experimental data is 5.1 ± 0.5 in phase I at 180 K.

The increase in isochoric thermal conductivity with increasing temperature was observed by our group earlier for cyclic compounds such as benzene C_6H_6 [3] and the “plastic” phase of cyclohexane C_6H_{12} [4]. In furan the effect is more pronounced, which may be associated with a stronger weakening effect of the TO interaction. It has been earlier shown that experimental data can be interpreted in the approximation of relaxation times within a model in which the heat is transported by low-frequency phonons and by “diffusive” modes above the phonon mobility edge [1,4].

Usually the thermal conductivity can be described within the framework of the Debye model [14]:

$$\Lambda = \frac{\hbar^2}{2\pi^2 v^2 k_B T^2} \int_0^{\omega_D} l_\Sigma(\omega) \omega^4 \frac{e^{\hbar\omega/(k_B T)}}{(e^{\hbar\omega/(k_B T)} - 1)^2} d\omega, \quad (1)$$

where v is the sound velocity, ω_D is the Debye frequency, $\omega_D = v(6\pi^2 n)^{1/3}$, $l_\Sigma(\omega)$ is the effective phonon mean free path determined by the all scattering mechanisms:

$$l_\Sigma(\omega) = \left(\sum_i l_i(\omega) \right)^{-1}. \quad (2)$$

In molecular crystals, the phonons participating in the heat transport are scattered by both phonons and rotational excitations. The corresponding mean free path for the Umklapp, one- and two-phonon scattering processes are [14,15].

$$l_u(\omega) = v/A\omega^2 T, \quad l_1(\omega) = \rho v^5/B^2 \Lambda_{\text{rot}} T \omega^2,$$

$$l_{II}(\omega) = \pi \rho^2 v^8/C^2 k_B C_{\text{rot}} T^2 \omega^4, \quad (3)$$

where A is a coefficient responsible for phonon–phonon scattering, B and C are constants of noncentral molecular interaction, Λ_{rot} and C_{rot} are the thermal conductivity and the heat capacity of the rotational subsystem, respectively; ρ is the density. It is assumed that $B = C^2$ in the first approximation [15]. The thermal conductivity of the rotational subsystem C_{rot} can be calculated from the known gas-kinetic expression: $\Lambda_{\text{rot}} = C_{\text{rot}} a^2 \tau^{-1}/3$, where a is the intermolecular distance, and τ is the characteristic time of the site-to-site transport of the rotational energy. It can be estimated as a mean period of the librations in furan (we borrowed the value $\tau = 1.3 \cdot 10^{-12}$ s) in accordance with [7]. Taking into account the Eqs. (2), (3), the phonon mean free path in the orientationally-disordered phase of molecular crystal can be written as

$$l_\Sigma(\omega) = \left(\frac{AT\omega^2}{v} + \frac{B^2 \Lambda_{\text{rot}} T \omega^2}{\rho v^5} + \frac{C^2 k_B C_{\text{rot}} T^2 \omega^4}{\pi \rho^2 v^8} \right)^{-1}. \quad (4)$$

When the temperature goes up, the phonon mean free path decreases and can become comparable with the wavelength. It is assumed that the total mean free path is restricted to a distance close to half the phonon wavelength: $\alpha\lambda/2 = \alpha\pi v/\omega$, where α is a numerical factor of the order of unity:

$$l(\omega) = \begin{cases} l_\Sigma(\omega), & 0 \leq \omega \leq \omega_0, \\ \alpha\pi v/\omega = \alpha\lambda/2, & \omega_0 < \omega \leq \omega_D. \end{cases} \quad (5)$$

In this case the vibrational spectrum is subdivided into two parts presenting the modes whose mean free paths are larger than $\alpha\lambda/2$ (phonons) and the “diffusive” modes

whose mean free paths reached $\alpha\lambda/2$. The value of ω_0 follows from Eqs. (4) and (5):

$$\omega_0 = -\frac{u}{(-\eta + \sqrt{u^3 + \eta^2})^{1/3}} + (-\eta + \sqrt{u^3 + \eta^2})^{1/3},$$

where parameters u and η are

$$u = \frac{\pi\rho^2v^7}{3C^2k_B C_{\text{rot}}T} \left(A + \frac{B^2\Lambda_{\text{rot}}}{\rho v^4} \right), \quad \eta = -\frac{\rho^2v^7}{2\alpha C^2k_B C_{\text{rot}}T^2}. \quad (7)$$

The integral (1) splits into two parts describing the contributions to the thermal conductivity from low-frequency phonons and high-frequency “diffusive” modes:

$$\Lambda = \Lambda_{\text{ph}} + \Lambda_{\text{dif}}, \quad (8)$$

where

$$\Lambda_{\text{ph}} = \frac{\hbar^2}{2\pi^2v^2k_B T^2} \int_0^{\omega_0} l_{\Sigma}(\omega)\omega^4 \frac{e^{\hbar\omega/(k_B T)}}{(e^{\hbar\omega/(k_B T)} - 1)^2} d\omega,$$

$$\Lambda_{\text{dif}} = \frac{\alpha\hbar^2}{2\pi v k_B T^2} \int_{\omega_0}^{\omega_D} \omega^3 \frac{e^{\hbar\omega/(k_B T)}}{(e^{\hbar\omega/(k_B T)} - 1)^2} d\omega. \quad (9)$$

The results were fitted to smoothed values of the thermal conductivity for the highest-density sample with $V_m = 58.76 \text{ cm}^3/\text{mole}$. The Debye temperature (99 K) and the sound velocity (1520 m/s) have been evaluated from the low-temperature heat capacity data [5] in the assumption that only translational modes contribute to it below 18 K. It

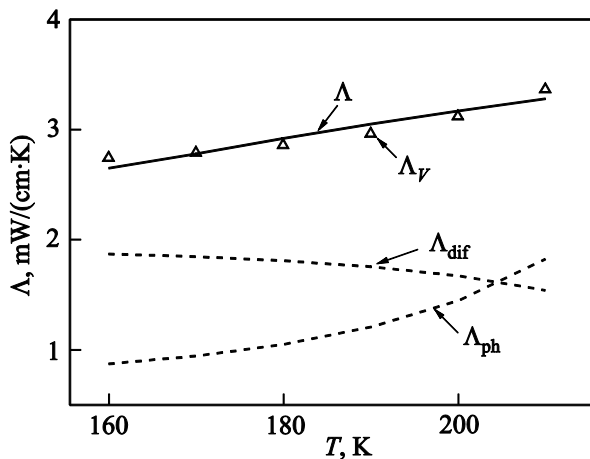


Fig. 4. The curve fitted to the smoothed experimental thermal conductivity of sample N3 (solid line) and the calculated contributions to thermal conductivity from low-frequency phonons Λ_{ph} and “diffusive” modes Λ_{dif} .

was assumed that C_{rot} varies linearly from $3R$ to $1.5R$ during over the orientationally disordered phase. The best agreement with the experimental results was achieved with $\alpha = 1.82$, $A = 1.01 \cdot 10^{-17} \text{ s/K}$, $B = 4.16$ and $C = 1.73$.

The curve fitted to the smoothed values the experimental thermal conductivity and the contributions to the thermal conductivity from low-frequency phonons Λ_{ph} and “diffusive” modes Λ_{dif} calculated by Eqs. (9) are shown in Fig. 4. The contribution of “diffusive” modes immediately after the phase transition is about twice as large as that of phonons. As the temperature goes up, the contribution of “diffusive” modes decreases and that of phonons increases, because the scattering of phonons by short-range orientational order fluctuations becomes weaker due to decreasing the TO interaction.

Conclusions

The isochoric thermal conductivity of solid furan has been investigated on three samples of different densities in the temperature interval from 140 K to the onset of melting. As temperature increases, isochoric thermal conductivity Λ_V in phase I increases gradually, while the isobaric one decreases smoothly. In cyclic hydrocarbons at premelting temperatures such behavior has been previously observed in benzene C_6H_6 [3] and cyclohexane C_6H_{12} [4]. The increase in isochoric thermal conductivity is most clearly expressed in furan, where the atoms in the ring plane are not equivalent. The effect can be associated with a stronger weakening of the TO interaction in furan as compared with C_6H_6 and C_6H_{12} . The experimental results are described within the Debye model of thermal conductivity in the approximation of the corresponding relaxation times and allow for the fact that the mean free path of phonons cannot become smaller than half the phonon wavelength. On this consideration the heat is transported by both phonons and “diffusive” modes.

Acknowledgments

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