

Phonon scattering and heat transfer by “diffusive” modes in solid C_6H_6 *

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The isochoric thermal conductivity of solid C_6H_6 is described within a model in which the heat is transferred by phonons and above the phonon mobility edge by “diffusive” modes migrating randomly from site to site. The mobility edge ω_0 is found from the condition, that the phonon mean-free path restricted by the examined mechanisms of scattering cannot become smaller than half the wavelength. The contributions of phonon-phonon, one and two-phonon scattering to the total thermal resistance of solid C_6H_6 are calculated under the assumption of additive contribution of different scattering mechanisms. Significant deviations from the dependence $\Lambda \propto 1/T$ are explained by thermal conductivity approaching its lower limit.

Key words: *molecular crystals, heat transfer, phonons, librons*

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1. Introduction

At low temperatures, well below the Debye temperature of solids (Θ_D), heat transport in simple molecular crystals is adequately described by basic theoretical models [1]. However, in high temperature region ($T \geq \Theta_D$) experimental and theoretical understanding of thermal conductivity of molecular crystals remains incomplete. For example, at $T \geq \Theta_D$, the classical theoretical models of heat transfer [1] predicted that thermal conductivity should be inversely proportional to temperature ($\Lambda \propto 1/T$), whereas experimental investigations of thermal conductivity of molecular crystals show considerable deviations from the above dependence [2]. Essentially all the basic concepts of heat transfer were created based on the studies of the simplest crystalline structure, i.e., atomic crystals. Therefore, the features typical of molecular crystals were not taken into account therein. One of the features that can affect the temperature dependence of thermal conductivity is the translation-rotation coupling. In the present study we wish to emphasize that thermal conductivity approaching its lower limit turns out to be another factor capable of determining the temperature dependence of thermal conductivity.

The purpose of this paper was to study the basic features of heat transfer in molecular crystals at $T \geq \Theta_D$. Our previous measurements have revealed a considerable deviation of the isochoric thermal conductivity of solid C_6H_6 from the dependence $1/T$ [2]. The effect was explained qualitatively but we did not provide a quantitative interpretation. The present work continues investigating the observed effect on the solid C_6H_6 . In the current study we analysed the temperature dependence of isochoric thermal conductivity of C_6H_6 using the model, which assumes that the heat is transferred by low-frequency phonons and above the mobility edge by “diffusive” modes, and taking into account phonon-phonon and phonon-rotation scattering.

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2. The object

Solid benzene under the pressure of its own saturated vapor has only one crystallographic modification: it has the orthorhombic spatial symmetry P_{bca} (D_{2h}^{15}) with four molecules per unit cell [3,4]. Benzene melts at 278.5 K and the melting-caused change in the entropy is $\Delta S_f/R = 4.22$ [5], which is much higher than Timmermans criterion for orientationally disordered phases. Here R is universal gas constant. The high-temperature magnitude of the Debye temperature of C_6H_6 is 120 K [6]. In the interval 90–120 K the second NMR moment of C_6H_6 drops considerably as a result of the molecule reorientations in the plane of the ring around the sixfold axis [7]. The activation energy of reorientational motion estimated from the spin-lattice relaxation time is 0.88 kJ/mole. The frequency of molecular reorientations at 85 K is 10^4 s⁻¹. On a further rise of the temperature it increases considerably, reaching 10^{11} s⁻¹ near melting temperature. The basic frequency of the benzene molecule oscillations about the sixfold axis at 273 K is $1.05 \cdot 10^{12}$ s⁻¹ [8].

At present, the thermal conductivity of solid C_6H_6 has been experimentally studied in the temperature range from 80 K to the melting temperature [2]. The isobaric thermal conductivity of solid C_6H_6 was also measured under the pressure above 100 MPa [9].

3. Model

The calculation was performed based on the Debye's expression for thermal conductivity [1] using the approach of Roufosse and Klemens [10] who used the idea of a lower limit for the phonon mean free path:

$$\Lambda = \frac{k_B}{2\pi^2 v^2} \int_0^{\omega_D} l(\omega) \omega^2 d\omega, \quad (1)$$

where v is the polarization-averaged sound velocity, ($\omega_D = (6\pi^2)^{1/3} v/a$) is the Debye frequency, a^3 is the volume per atom (molecule), and $l(\omega)$ is the phonon mean-free path.

Heat transfer in molecular crystals at $T \geq \Theta_D$ is determined mainly by phonon-phonon and phonon-rotational interactions. We assumed that the phonon-rotation relaxation time is determined by the one and two-phonon scattering processes [11]. Then, $l(\omega)$ – the combined phonon mean-free path determined by all of the examined mechanisms of scattering can be written as:

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

To explain the behavior of the thermal conductivity in solid CH_4 and CD_4 , the authors of [11] used the analogy between molecular and spin systems. In a number of magnetic crystals the thermal conductivity was observed to increase above the magnetic phase transition. The reason for these anomalies is the scattering of phonons by critical fluctuations of the short-range magnetic order above the Neel point. In molecular crystals an increase of the isochoric thermal conductivity with increasing temperature is due to the weakening of phonon scattering by fluctuations of the short-range orientational order. By analogy, using the equations for one and two-phonon relaxation times [12], the phonon mean free path of each of the examined scattering mechanisms can be expressed as:

$$l_u(\omega) = v/AT\omega^2, \quad (3)$$

$$l_I(\omega) = \rho v^5/B^2 \Lambda_{rot} T \omega^2, \quad (4)$$

$$l_{II}(\omega) = \pi \rho^2 v^8/C^2 k_B C_{rot} T^2 \omega^4, \quad (5)$$

$$A = \frac{18\pi^3}{\sqrt{2}} \frac{k_B \gamma^2}{m a^2 \omega_D^3}, \quad (6)$$

where the Grüneisen parameter $\gamma = -(\partial \ln \Theta_D / \partial \ln V)_T$, $l_u(\omega)$ is the phonon mean-free path determined by U -processes, $l_I(\omega)$ and $l_{II}(\omega)$ are the phonon mean-free paths for one and two-phonon

scattering, respectively, m is the average atomic (molecular) weight, B and C are the constants of non-central intermolecular interactions, Λ_{rot} is thermal conductivity of the orientational subsystem, C_{rot} is rotational heat capacity per unit volume. In the first approximation: $B = C^2$ [11]. The coefficient B can be found from the pressure dependence of melting temperature:

$$B = - \left(\frac{1}{\chi_T} \right) \frac{\partial (\ln T_f)}{\partial P}, \quad (7)$$

where χ_T is the isothermal compressibility, T_f is temperature of the phase transition, P is pressure. Thermal conductivity Λ_{rot} can be found from the well-known gas-kinetic expression:

$$\Lambda_{\text{rot}} = \frac{1}{3} C_{\text{rot}} a^2 \tau^{-1}, \quad (8)$$

where τ is the characteristic time of orientational excitation transfer from one lattice site to another. This time was estimated from the relation $\tau \approx \hbar/\Delta E$ [13], where non-central part ΔE of the intermolecular interaction was calculated based on the expression given in [14] relating it to the phase transition temperature of C₆H₆.

By substituting (3)–(5) in (2), the combined phonon mean-free path can be expressed as follows:

$$l_{\Sigma}(\omega) = \left(\frac{AT\omega^2}{v} + \frac{B^2\Lambda_{\text{rot}}T\omega^2}{\rho v^5} + \frac{C^2 k_B C_{\text{rot}} T^2 \omega^4}{\pi \rho^2 v^8} \right)^{-1}. \quad (9)$$

Expression (9) is not applicable if $l(\omega)$ becomes of the order of or smaller than half the phonon wavelength: $\lambda/2 = \pi v/\omega$. A similar situation was considered previously for the case of U -processes alone [15]. Let us assume that in the general case:

$$l(\omega) = \begin{cases} l_{\Sigma}(\omega), & 0 \leq \omega \leq \omega_0, \\ \alpha \pi v/\omega = \alpha \lambda/2, & \omega_0 < \omega \leq \omega_D, \end{cases} \quad (10)$$

where α is the numerical coefficient of the order of unity. The frequency ω_0 can be found from the condition:

$$\left(\frac{AT\omega_0^2}{v} + \frac{B^2\Lambda_{\text{rot}}T\omega_0^2}{\rho v^5} + \frac{C^2 k_B C_{\text{rot}} T^2 \omega_0^4}{\pi \rho^2 v^8} \right)^{-1} = \frac{\alpha \pi v}{\omega_0}. \quad (11)$$

It is equal to

$$\omega_0 = - \frac{u}{\left(-\eta + \sqrt{u^3 + \eta^2} \right)^{1/3}} + \left(-\eta + \sqrt{u^3 + \eta^2} \right)^{1/3}, \quad (12)$$

where the parameters u and η are:

$$u = \frac{\pi \rho^2 v^7}{3 C^2 k_B C_{\text{rot}} T} \left(A + \frac{B^2 \Lambda_{\text{rot}}}{\rho v^4} \right); \quad \eta = - \frac{\rho^2 v^7}{2 \alpha C^2 k_B C_{\text{rot}} T^2}. \quad (13)$$

The condition (11) is the well-known Ioffe-Regel criterion which implies localization. Therefore, we can assume that the excitations whose frequencies are above the phonon mobility edge ω_0 are “localized” or “diffusive”. Since completely localized modes do not contribute to the thermal conductivity, we supposed that the localization is weak and the excitations are capable of hopping from site to site diffusively, as was suggested by Cahill and Pohl [16].

If $\omega_0 > \omega_D$ the mean free path of all modes exceeds $\lambda/2$ and the thermal conductivity is determined exceptionally by the processes of phonon scattering. At $\omega_0 \leq \omega_D$ the integral of thermal conductivity (1) is subdivided into two parts describing the contributions to the heat transfer from the low-frequency phonons and high-frequency “diffusive” modes:

$$\Lambda = \Lambda_{\text{ph}} + \Lambda_{\text{dif}}. \quad (14)$$

In the high-temperature limit ($T \geq \Theta_D$) these contributions are:

$$\Lambda_{\text{ph}} = \frac{k_B}{2\pi^2 v^2} \int_0^{\omega_0} \frac{\omega d\omega}{\frac{C^2 k_B C_{\text{rot}} T^2 \omega^3}{\pi \rho^2 v^8} + \frac{AT\omega}{v} + \frac{B^2 \Lambda_{\text{rot}} T \omega}{\rho v^5}}, \quad (15)$$

$$\Lambda_{\text{dif}} = \frac{\alpha k_B}{4\pi v} (\omega_D^2 - \omega_0^2). \quad (16)$$

In the case of orientationally ordered phases equation (15) gives the well-known dependence $\Lambda \propto 1/T$ at $\omega_0 > \omega_D$.

$$\Lambda_{\text{ph}} = \frac{k_B \omega_D}{2\pi^2 v AT}. \quad (17)$$

4. Results and discussion

As was mentioned above, at temperature close to or above the Debye temperature $T \geq \Theta_D$ the thermal conductivity of pure crystals should be inversely proportional to temperature [1]. To obey the law $1/T$, the volume of the crystals should remain invariable, because the modes would otherwise change and so would the temperature dependence of the thermal conductivity [9,17].

Nevertheless, isochoric studies of thermal conductivity of molecular crystals [2,15,18] show a considerable deviation from this law. These discrepancies may be due to the thermal conductivity approaching its lower limit. The concept of the lower limit of thermal conductivity is based on the following: the mean free paths of the oscillatory modes participating in heat transfer are essentially limited but it cannot become smaller than half the phonon wavelength $\lambda/2$, and the site-to-site heat transport proceeds as a diffusive process [10]. In this case the lower limit of the lattice thermal conductivity Λ_{min} can be written as [16]:

$$\Lambda_{\text{min}} = \left(\frac{\pi}{6}\right)^{\frac{1}{3}} k_B n^{\frac{2}{3}} \sum_i v_i \left\{ \left(\frac{T}{\Theta_i}\right)^2 \int_0^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \right\}. \quad (18)$$

The summation is over three (one longitudinal and two transverse) sound modes with the sound velocities v_i . Θ_i is the Debye cut-off frequency for each polarization in Kelvin's: ($\Theta_i = v_i (\hbar/k_B) (6\pi^2 n)^{1/3}$), $n = 1/a^3$ is the number of atoms per unit volume.

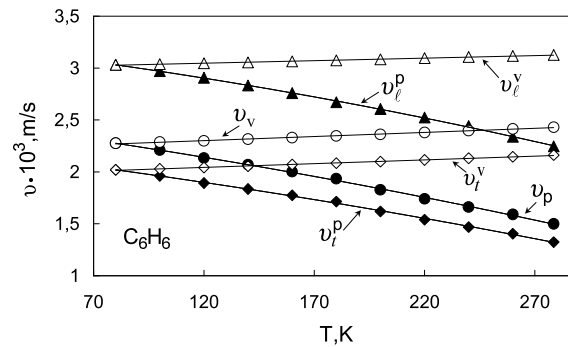


Figure 1. Calculated temperature dependence of the isobaric and isochoric ($V_{\text{mol}}=70.5 \text{ cm}^3/\text{mole}$) sound velocities of solid C_6H_6 . v_p, v_ℓ^p, v_t^p and v_v, v_ℓ^v, v_t^v are mean, longitudinal, and transversal phonon velocities for isobaric and isochoric conditions, respectively.

The calculated values of Λ_{min} were as a rule considerably smaller than the experimental ones [2,15,18]. The most obvious reason for this difference is that the site to site transfer of the rotational energy was not taken into account. In molecular crystals the heat is transferred by mixed

translation-rotation modes, whose heat capacity is saturated in proportion to the total molecular degree of freedom. Taking into account these features of molecular crystals, the lower limit of the thermal conductivity can be represented as [15]:

$$\Lambda_{\min}^* = \frac{1}{2} \left(\frac{\pi}{6} \right)^{\frac{1}{3}} \left(1 + \frac{z}{3} \right) k_B n^{\frac{2}{3}} (v_\ell + 2v_t), \quad (19)$$

where v_ℓ and v_t are the longitudinal and transversal sound velocities, respectively, z is the number of rotational degree of freedom.

To our knowledge, no experimental data are available on the sound velocity of solid C₆H₆. In this respect, it was calculated using the method described in [19]. The necessary data were taken from [20,21]. Figure 1 shows the calculated sound velocity of solid C₆H₆. The isochoric speed of sound corresponds to the molar volume $V_{\text{mol}}=70.5 \text{ cm}^3/\text{mole}$.

The heat capacity of molecular crystal can be written as a sum of contributions from the translational C_{tr} and rotational C_{rot} subsystems and a contribution due to the intramolecular vibrations of the atoms C_{in} :

$$C_V = C_{\text{tr}} + C_{\text{rot}} + C_{\text{in}}. \quad (20)$$

To separate the partial contributions to the heat capacity, we used the method described in [22]. The heat capacity at constant volume C_V is difficult to measure. In practice, it is recalculated, when data on thermal expansion β [20] and Grüneisen parameter γ [6] are available, from the values of the heat capacity at atmospheric pressure C_p [23] by using the known thermodynamic relation:

$$C_V = \frac{C_p}{(1 + \gamma\beta T)}, \quad (21)$$

C_{tr} was calculated in the Debye approximation using the characteristic temperature $\Theta_D = 120 \text{ K}$ obtained from the expression

$$\Theta_D = v (\hbar/k_B) (6\pi^2 n)^{\frac{1}{3}}$$

and is close to $3R$. C_{in} was calculated in the Einstein approximation using the intramolecular vibrational frequencies ν_i [6]. C_{rot} was determined as $C_{\text{rot}} = C_V - C_{\text{tr}} - C_{\text{in}}$. Our results for components of the heat capacity are shown in figure 2. The heat capacity of librational subsystem C_{rot} constantly increases with the temperature increase, and at premelting temperatures approaching the values that are considerably larger than $3/2R$, which is characteristic of a free three-dimensional rotator.

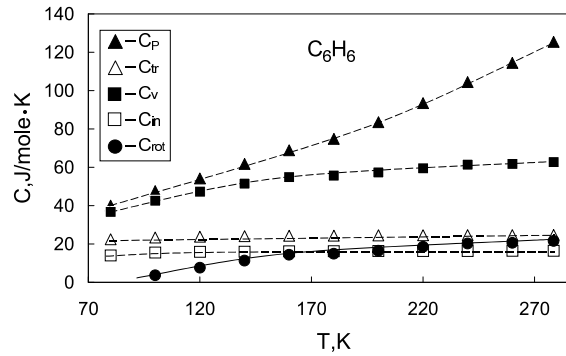


Figure 2. Temperature dependence of the heat capacity contributions in solid C₆H₆: C_p show the data [23] on the heat capacity at constant pressure, while C_{in} , C_{tr} , and C_{rot} correspond to the calculated curves for the heat capacity at constant molar volume $V_{\text{mol}}=70.5 \text{ cm}^3/\text{mole}$ and for the intramolecular, translational, and rotational components of the heat capacity C_V , respectively.

To correctly compare the experimental results of thermal conductivity with the theory it is necessary to use data at constant density to exclude the effect of thermal expansion. The isochoric thermal conductivity of C₆H₆ ($V_{\text{mol}}=70.5 \text{ cm}^3/\text{mole}$) according to [2] is shown in figure 3

(squares). The behavior of isochoric thermal conductivity Λ_v of solid benzene is inconsistent with the theoretical prediction. Satisfactory agreement with the classical law $1/T$ is observed only below 180 K ($\Lambda_v \sim T^{-0.8}$). At $T > 180$ K, Λ_v is practically constant and even starts to grow slightly at premelting temperatures.

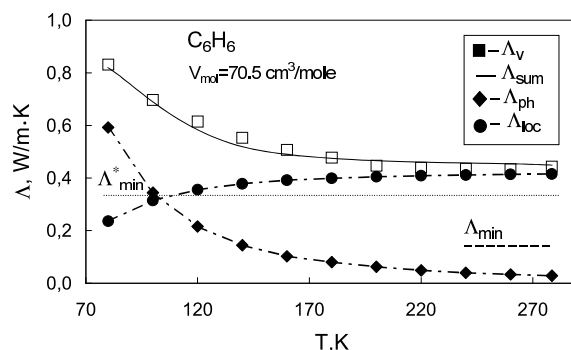


Figure 3. Isochoric thermal conductivity Λ_v of solid C_6H_6 (squares) [2]. The solid line is the fitting curve for isochoric thermal conductivity. Λ_{ph} and Λ_{dif} are contributions of phonons and “diffusive” modes to heat transfer, respectively. The lower limits of the thermal conductivity Λ_{min} and Λ_{min}^* calculated according to equations (18), (19).

The computer fitting of the thermal conductivity using equations (12)–(16) was performed using the least square method, varying the coefficients A, B, C , and α . The parameters of the Debye model for thermal conductivity used in the fitting (a, v), and the fitted values A, B, C , and α are listed in table 1.

Table 1. Parameters of the Debye model of thermal conductivity used in the fitting, and other quantities which were used for calculation.

$V_{mol}, \text{ cm}^3/\text{mole}$	$a, 10^{-8} \text{ cm}$	$v, \text{ m/s}$	γ	α	$A, 10^{-17} \text{ s/K}$	B	C
70.5	4.9	2275	3.3	4.4	7.6	6.8	2.6

The fitting results for isochoric thermal conductivity are shown in figure 3 (solid line). The same figure shows the contributions (dot-and-dash lines) to the heat transfer from the low-frequency phonons Λ_{ph} and the high-frequency “diffusive” modes Λ_{dif} (calculated by equations (15), (16)). The dotted line shows the lower limit of thermal conductivity Λ_{min}^* (19) calculated taking into account the possibility of site to site rotational energy transfer. The dashed line in the lower part of the figure is the lower limit of thermal conductivity Λ_{min} (18) calculated according to Cahill and Pohl within the framework of the Einstein model for the diffusive transfer of heat directly from atom to atom [16].

It is seen (figure 3) that the “diffusive” behavior of oscillatory modes appears prior to 70 K. As temperature rises, the amount of heat transferred by the “diffusive” modes increases, and at 110 K it becomes equal to the heat transferred by the low-frequency phonons. Above 150 K most of the heat is transported by the “diffusive” modes. As demonstrated in figure 3, our theoretical findings for thermal conductivity agree well with experimental data cited in [2]. The discussion of the lower limit of thermal conductivity of molecular crystals brings up inevitable question: should the site-to-site transport of the rotational energy of the molecules be taken into account? The minimum values of the experimental thermal conductivity Λ_v is 1.2 times higher than Λ_{min}^* calculated by equation (19), and 2.5 times higher than Λ_{min} calculated by equation (18). The above correlation between the Λ_{min} and Λ_{min}^* suggests a positive answer.

In high temperature region of existence of molecular crystals the contribution of librions Λ_{rot} to the heat transfer is assumed to be relatively small [2,15,24]. The calculation of Λ_{rot} according to (8) gives the values $1.42 \cdot 10^{-3} \text{ W/m}\cdot\text{K}$ at $T=80$ K and $1.5 \cdot 10^{-2} \text{ W/m}\cdot\text{K}$ at $T=278$ K. These

results prove the above assumption. At the same time, the role of librations in scattering processes is important [2,24,25].

To answer questions as to basic peculiarities of phonon-rotational coupling in the solid C₆H₆, we have undertaken to separate the phonon-phonon and phonon-rotational contributions to the total thermal resistance. A number of molecular crystals have several solid phases, which substantially differ in the character of orientational ordering. If the non-central forces are strong and the temperature is low, there is a long-range orientational order in the location of molecular axes. The molecules perform small vibrations around the selected axes (librations), so that the motion of the neighbouring molecules is correlated and the collective orientation excitations (librons) propagate in the crystal. In the first approximation, the translation-orientation interaction in molecular crystals leads to an additional contribution to the thermal resistance $W=1/\Lambda$ [17].

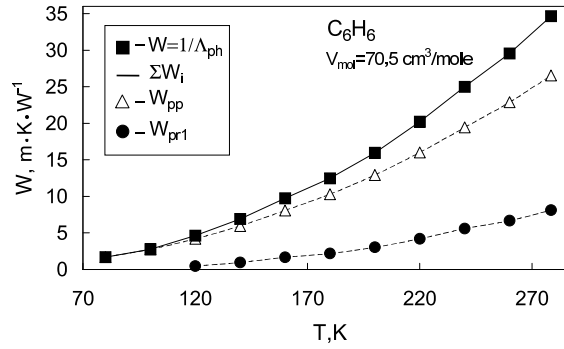


Figure 4. Contributions of the phonon-phonon scattering W_{pp} , and one-phonon W_{pr1} mechanisms of scattering to the total thermal resistance of solid C₆H₆. Square symbols indicate total thermal resistance $W=1/\Lambda_{ph}$. The solid line shows the sum of thermal resistances W_{pp} , W_{pr1} , and W_{pr2} .

If the noncentral forces are relatively weak, and the temperature is high enough, the molecules can have a considerable orientational freedom. In this case a number of orientations are accessible to the molecule, which can pass from one orientation to another. In individual cases the limit of such reorientational motion can be a continuous rotation. The additional phonon scattering (compared to the phonon-phonon one) may originate in molecular crystals due to the collective rotational motion of molecules. As a rule, the unfreezing of molecular rotation is accompanied by an increase of the isochoric thermal conductivity due to the weakening of phonon-rotational scattering [2,15]. We assume that the contributions of different scattering mechanisms to the thermal resistance are additive [1]:

$$\sum_i W_i = W_{pp} + W_{pr1} + W_{pr2}, \quad (22)$$

where W_{pp} is the phonon-phonon thermal resistance, W_{pr1} and W_{pr2} are thermal resistances determined by one and two-phonon mechanisms of phonon-rotational scattering, respectively. Using (1) and (3)–(5) we have:

$$W_{pp} = 2\pi^2 \nu AT \left(k_B \int_0^{\omega_0} d\omega \right)^{-1}, \quad (23)$$

$$W_{pr1} = 2\pi^2 B^2 \Lambda_{rot} T \left(k_B v^3 \rho \int_0^{\omega_0} d\omega \right)^{-1}, \quad (24)$$

$$W_{pr2} = 2\pi C^2 T^2 C_{rot} \left(v^6 \rho^2 \int_0^{\omega_0} \frac{d\omega}{\omega^2} \right)^{-1}. \quad (25)$$

Figure 4 shows the calculated results for thermal resistance C_6H_6 . The total thermal resistance $W=1/\Lambda_{ph}$ is shown with black squares. The solid curve is the sum $\sum_i W_i$ of the thermal resistances, calculated by equations (23)–(25). The phonon-phonon component of the thermal resistance W_{pp} increases with temperature. As temperature rises the thermal resistance W_{pr1} due to the one-phonon scattering at rotational excitations of molecules also increases and becomes substantial after 120 K. The two-phonon component W_{pr2} of the total thermal resistance is practically zero (it does not exceed $5 \cdot 10^{-5} m \cdot K/W$). From the aforesaid, it is clear that phonon-rotation scattering cannot be a reason for an increase of isochoric thermal conductivity of C_6H_6 .

5. Conclusions

It is shown that the isochoric thermal conductivity of C_6H_6 can be described in a model, where the heat is transferred by phonons and above the phonon mobility edge by “diffusive” modes migrating randomly from site to site and taking into account the transfer of rotational energy between lattice sites. The total thermal resistance in molecular crystals is determined by phonon-phonon and phonon-rotation scattering mechanisms. In turn, the phonon-rotation relaxation time is determined by the one and two-phonon scattering. The contributions of phonon-phonon, one and two-phonon scattering to the total thermal resistance of solid C_6H_6 are calculated in supposition of additive contribution of different scattering mechanisms.

Based on these studies, it seems justified to conclude that the main reason for the essential deviations of the isochoric thermal conductivity of C_6H_6 from the dependence $1/T$ is the additional heat transfer by “diffusive” modes. The latter is caused by the thermal conductivity approaching its lower limit.

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Фононне розсіяння та перенесення тепла “дифузними” модами в твердому C₆H₆

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Ізохорна теплопровідність твердого C₆H₆ описується в рамках моделі, в якій тепло переноситься фононами, а вище від граничної рухливості – “дифузними” модами, що мігрують випадковим чином з вузла на вузол. Границя фононної рухливості ω_0 знаходиться із умови, що довжина вільного пробігу фононів, котра визначається розглянутими механізмами розсіяння фононів, не може стати меншою половини довжини хвилі. Внески фонон-фононного, одно та дво-фононного розсіяння в повний тепловий опір твердого C₆H₆ розраховано в припущенні адитивності внесків різних механізмів фононного розсіяння. Значні відхилення від залежності $\Lambda \propto 1/T$ пояснюються наближенням теплопровідності до її нижньої границі.

Ключові слова: молекулярні кристали, перенос тепла, фонони, ліброни

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