Translation-rotation coupling and heat transfer in orientationally-disordered phase of CCl$_4$

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Abstract: The isochoric thermal conductivity of an orientationally-disordered phase of CCl$_4$ is analysed within a model in which 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 cannot become smaller than half the phonon wavelength. The contributions of phonon-phonon, one-, and two-phonon scattering to the total thermal resistance of solid CCl$_4$ are calculated under the assumption that the different scattering mechanisms contribute additively. An increase in the isochoric thermal conductivity with temperature is explained by suppression of phonon scattering at rotational excitations due to a decrease in correlation in the rotation of neighbouring molecules.
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1 Introduction

Theoretical models of heat transfer in solid dielectrics have predicted the thermal conductivity behaviour $\Lambda \propto 1/T$ at temperatures $T \geq \Theta_D$ (Θ_D is the Debye temperature) [1]. However, the thermal conductivity of molecular crystals shows considerable deviations from the above dependence [2–5]. At present, there is no generally accepted theory that

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would adequately describe the experimental thermal conductivity of molecular crystals in the high temperature region. Essentially all of the basic concepts of heat transfer were created mainly on the basis of studies of the simplest crystalline structure: atomic crystals. Therefore, features typical for molecular crystals were not taken into account in them. One of these features that can affect the temperature dependence of the thermal conductivity is translation-rotation coupling. In molecular crystals the heat transfer is determined by both the translational and rotational motions of molecules at the lattice sites. As the temperature rises, the rotational motion of the molecules in crystals can have basically the following stages: an increase in the libration amplitude, jump-like re-orientation of the molecules, increasing frequency of reorientations, hindered rotations of the molecules, and, finally, nearly free rotation of the molecules. A consequence of strong rotation-translation coupling is to lead to additional phonon scattering. It should be noted that the additional factor which can determine the temperature dependence of the thermal conductivity at $T \geq \Theta_D$ also causes the thermal conductivity to approach its lower limit [4].

The purpose of this paper was to study basic features of heat transfer in the orientationally disordered (OD) phase of CCl_4. Our previous measurements have revealed an increase of isochoric thermal conductivity of solid CCl_4 above 200 K (in "normal" and OD phases) [5]. The effect was explained qualitatively but we did not provide a quantitative interpretation. The present work continues the investigation of the observed phenomenon. In the current study we analyzed the temperature dependence of isochoric thermal conductivity of CCl_4 in the OD phase by using a model that assumed that the heat is transferred by low-frequency phonons, above the mobility edge by "diffusive" modes, and taking into account phonon-phonon and phonon-rotation scattering.

2   The object

Carbon tetrachloride has an interesting feature: on cooling to 250.3 K liquid CCl_4 crystallizes into a face-centred cubic (fcc) form (Ia) with four molecules per unit cell, which at a further decrease in temperature by some number of degrees transforms into a rhombohedral phase (Ib) with 21 molecules per unit cell [6, 7]. Below 225.5 K the rhombohedral phase transforms into a monoclinic one in the space symmetry group $C2/c - (C_{2h}^6)$ with Z=32. On heating, the low-temperature phase (II) always changes to the rhombohedral form. Because of low entropy of melting $\Delta S_f/R$ =1.21, the phase (Ib) of CCl_4 may be classified as "plastic" [8].

The three forms of solid CCl_4 are closely related. The centres of mass of the molecules are only slightly shifted relative to their positions in the cubic and rhombohedral phases. Besides which, the molecular orientations in the phase (II) correlate closely with the directions of the highest-density distribution function in the phase (I). According to experimental data, the character of the molecular motion in the plastic phase of CCl_4 is closely similar to that in the liquid state. For example, for CCl_4 no discontinuities are observed in the curve of spin-spin relaxation time T_2 of ^{35}Cl on melting of the plastic phase [9] and

in the curve of the reorientational correlation time obtained from Raman line broadening [10, 11]. Zuk, Kiefte, and Clouter estimated the elastic constants of CCl$_4$ in the phase (I) by the Brillouin scattering method [12]. They detected an anomalously high (as compared to solid inert gases) ratio of sound velocities in the $< 110 >$ and $< 111 >$ directions and interpreted this as an indication of a strong translation-orientation interaction.

The thermal conductivity of solid CCl$_4$ had been measured at constant pressure in the temperature range 80-250 K [5, 13] and on several isochores above 200 K [14].

3   Model

An important common feature of simple molecular crystals is that in the condensed phases the intramolecular vibration frequencies ($\sim$1000 cm^{-1}) exceed by an order of magnitude the intermolecular ones (the corresponding lattice-mode frequencies are below$\sim$100 cm^{-1}), so they can be treated independently. In such an approximation each molecule participates in two types of motion: translational, when the molecular center of mass shifts, and rotational, when the center of mass rests. In general, translational and orientational motions are not independent of one another, but rather they occur as coupled translational - orientational vibrations [15–17].

In consequence of the complexity of description of such motion, a simplified model where the translational and orientational subsystem are described independently is often used [18–20]. In such a description it is assumed that the translational-orientational interaction results in a renormalization of the dispersion law and, correspondingly, the sound velocities. There are few theoretical works dedicated to influence of rotational motion on heat transfer in molecular crystals [21–24]. It has been universally accepted that the heat in molecular crystals is transferred by phonons, which are scattered by phonon-phonon and, additionally, by phonon-rotational interactions. In the orientationally-ordered phases of molecular crystals the rotational excitations are a collective phenomenon (librons) [18]. If only three-quasiparticle scattering is taken into account and the phonon mean-free path exceeds the phonon wavelength, the 1/T law should be asserted at $T \geq \Theta_D$ [21]. In the orientationally-disordered phases, however, the absence of the long-range orientational ordering suggests that well-defined librational modes cannot propagate in a crystal. Nevertheless, a short-range cooperative orientational motion of molecules prevails immediately above the phase transition in the OD phase, and it is damped out with increasing temperature [22–24]. If the phonon-rotational scattering decreases more rapidly then the phonon-phonon scattering increases, the thermal conductivity can grow.

The present calculations were performed on the basis of the standard Debye expression for thermal conductivity [1]:

$$\Lambda = \frac{k_B}{2\pi^2 \upsilon^2} \int\limits_0^{\omega_D} l(\omega)\omega^2 d\omega, \tag{1}$$

where υ is the polarization-averaged sound velocity, $l\left(\omega\right)$ is the phonon mean-free path, ω_D is the Debye frequency ($\omega_D = (6\pi^2)^{1/}3\upsilon/a$), and a is the lattice constant.

We assumed that the heat transfer in molecular crystals at $T \geq \Theta_D$ is determined by phonon-phonon and phonon-rotational interactions, and that the phonon-rotation relaxation time is described by one- and two-phonon scattering processes [22, 23]. Then, $l(\omega)$, the combined phonon mean-free path, can be written as:

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

To explain the behavior of the thermal conductivity in the orientationally disordered phases of solid methane and deuteromethane, the authors of [22] used the analogy between molecular and spin systems [25]. In a number of magnetic crystals the thermal conductivity was observed to increase above the magnetic phase transition. Reason for these anomalies is the scattering of phonons by critical fluctuations of the short-range magnetic order above the Neel point. In orientationally disordered phases of the molecular crystals an increase of the isochoric thermal conductivity with increasing temperature is due to weakening of phonon scattering by fluctuations of the short-range orientational order. By existing analogy, using the equations for one- and two-phonon relaxation times [22], the phonon mean free path of each of the examined scattering mechanisms can be expressed as:

$$l_u(\omega) = \upsilon \Big/ AT\omega^2,\tag{3}$$

$$l_I(\omega) = \rho\upsilon^5 \Big/ B^2 \Lambda_{\mathrm{rot}} T\omega^2,\tag{4}$$

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

$$A = \frac{18\pi^3}{\sqrt{2}} \frac{k_B \gamma^2}{ma^2\omega_D^3},\tag{6}$$

where the Grüneisen parameter $\gamma = -\left(\partial \ln \Theta_D / \partial \ln V\right)_T$, $l_u(\omega)$ 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 the thermal conductivity of the orientational subsystem, and C_{rot} is the rotational heat capacity per unit volume. In the first approximation: $B = C^2$ [22]. The coefficient B can be found from the pressure dependence of the orientational ordering temperature:

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

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

$$\Lambda_{\mathrm{rot}} = \frac{1}{3} C_{\mathrm{rot}} a^2 \tau^{-1},\tag{8}$$

where τ is the characteristic time of orientational excitation transfer from one lattice site to another. This time can be estimated from the relation $\tau \approx \hbar/\Delta E$ [26], where the

non-central part ΔE of the intermolecular interaction was calculated on the basic of the expression given in [23] relating it to the temperature of transition into the orientationally ordered phase of CCl_4.

By substituting (3, 4, 5) in (2), the combined phonon mean-free path can be expressed as:

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

We have also taken into account the next circumstance. Expression (9) is not applicable if $l(\omega)$ becomes of order or smaller than half the phonon wavelength: $\lambda/2 = \pi\upsilon/\omega$. A similar situation was considered previously for the case of U-processes alone [27]. Let us assume that in the general case:

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

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

$$\left(\frac{AT\omega_0^2}{\upsilon} + \frac{B^2\Lambda_{\mathrm{rot}}T\omega_0^2}{\rho\upsilon^5} + \frac{C^2 k_B C_{\mathrm{rot}}T^2\omega_0^4}{\pi\rho^2\upsilon^8} \right)^{-1} = \frac{\alpha\pi\upsilon}{\omega_0}, \tag{11}$$

It equals

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

where the parameters u and η are:

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

The condition (11) is the well-known Ioffe-Regel criterion which implies localization. We can therefore 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 can hop from site to site diffusively, as was suggested by Cahill and Pohl [28].

If the mean free path of all modes exceeds $\lambda/2$ the thermal conductivity is determined solely by the processes of phonon scattering. At $\omega_0 \le \omega_D$ 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:

$$\Lambda = \Lambda_{\mathrm{ph}} + \Lambda_{\mathrm{dif}}, \tag{14}$$

The validity of such description is supported by molecular dynamics simulations using the Green-Kubo method. Recently, the thermal transport in the Lennard-Jones argon

face centered cubic crystal was described by two time constants related to the decay of the heat current autocorrelation function [29]. The first time scale is associated with short wavelength acoustic phonons that have mean-free paths equal to one half of their wavelength. The second time scale is longer, and corresponds to acoustic phonons with mean-free paths longer than one half of their wavelength.

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

$$\Lambda_{\mathrm{ph}} = \frac{k_B}{2\pi^2 \upsilon^2} \int\limits_0^{\omega_0} \frac{\omega \, d\omega}{\frac{C^2 k_B C_{\mathrm{rot}} T^2 \omega^3}{\pi \rho^2 \upsilon^8} + \frac{AT\omega}{\upsilon} + \frac{B^2 \Lambda_{\mathrm{rot}} T\omega}{\rho \upsilon^5}}, \tag{15}$$

$$\Lambda_{\mathrm{dif}} = \frac{\alpha \, k_B}{4\pi \, \upsilon} \left(\omega_D^2 - \omega_0^2 \right), \tag{16}$$

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

$$\Lambda_{\mathrm{ph}} = \frac{k_B \omega_D}{2\pi^2 \upsilon \, AT}, \tag{17}$$

4   Results and discussion

As it was marked above, the thermal conductivity of molecular crystals should be inversely proportional to temperature at $T \geq \Theta_D$ if only three-quasiparticle scattering is taken into account. In actual fact, isochoric studies of the thermal conductivity of molecular crystals [4, 5, 14] detected a considerable deviation from this dependence. One of the reasons for these discrepancies is an approach of the thermal conductivity to its lower limit. The concept of the lower limit of thermal conductivity is based on following: the mean-free paths of all oscillatory modes participating in the heat transfer is equal to half the phonon wavelength $\lambda/2$, and the site-to-site heat transport proceeds as a diffusive process [28]. The lower limit of the lattice thermal conductivity Λ_{min} can be written as [28]:

$$\Lambda_{\mathrm{min}} = \left(\frac{\pi}{6} \right)^{1/3} k_B n^{2/3} \sum_i \upsilon_i \left\{ \left(\frac{T}{\Theta_i} \right)^2 \int\limits_0^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \right\}, \tag{18}$$

The summation is over three (one longitudinal and two transverse) sound modes with sound velocities υ_i, Θ_i is the Debye cutoff frequency for each polarization expressed in degrees K $(\Theta_i = \upsilon_i (\hbar/k_B) (6\pi^2 n)^{1/3})$, and $n = 1/a^3$ is the number of atoms per unit volume.

It was supposed that the rotational energy transfer should be taken into consideration in molecular crystals and the lower limit of the thermal conductivity can be rewritten at $T \geq \Theta_D$ as [4]:

$$\Lambda_{\mathrm{min}}^* = \frac{1}{2} \left(\frac{\pi}{6} \right)^{1/3} \left(1 + \frac{z}{3} \right) k_B n^{2/3} \left(\upsilon_\ell + 2\upsilon_t \right), \tag{19}$$

where υ_ℓ and υ_t are the longitudinal and transversal sound velocities, respectively, and z is the number of rotational degrees of freedom.

McGaughey and Kaviany [30] have also found on the example of silica-based crystals that optical phonons make a non-negligible contribution to the thermal conductivity when the total value is 10 W/m·K or lower. Two mechanisms have been identified. The first, which is short-range and linked to optical phonons and short-wavelength acoustic phonons, is related to the geometry of the crystal structure. The resulting thermal conductivity is temperature independent, and has been interpreted as a minimum value for the crystal phase. This limiting value is different from that predicted by available models based on a disordered structure. The second mechanism corresponds to the long-time propagation of acoustic phonons within a crystal. It accounts for the temperature dependence and majority of the magnitude of the thermal conductivity.
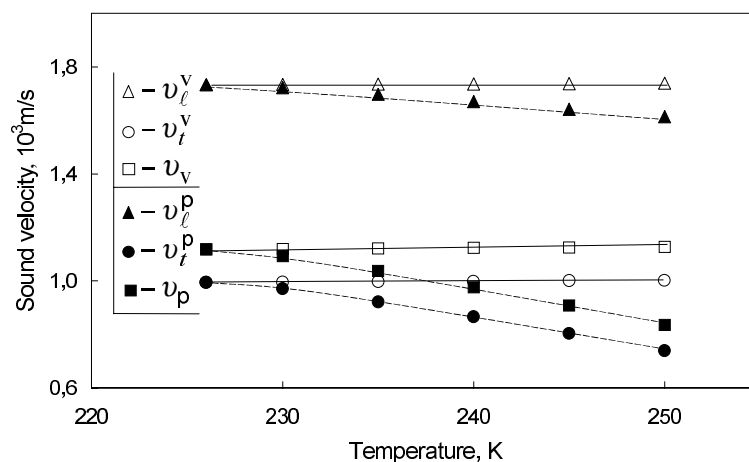

Fig. 1 Calculated temperature dependence of the isobaric and isochoric sound velocities of solid CCl$_4$. v_P, v_ℓ^P, v_t^P and v_V, v_ℓ^V, v_t^V are the mean, longitudinal, and transversal sound velocities for isobaric and isochoric conditions, respectively.

To our knowledge, no experimental data is available on the sound velocity of solid CCl$_4$. Because of this, the sound velocity was calculated by the method described in [31]. The necessary data were taken from [12, 14, 32]. Figure 1 shows the calculated sound velocities of solid CCl$_4$(Ib). The isochoric speeds of sound correspond to the molar volume V_{mol}=86.48 cm^3/mole.

The heat capacity of a molecular crystal can be written as a sum of contributions from the translational C$_{tr}$, rotational C$_{rot}$, and intramolecular C$_{in}$ vibrations [21]:

$$C_V = C_{tr} + C_{rot} + C_{in}, \tag{20}$$

To separate the partial contributions to the heat capacity, we used the method described in [33]. The heat capacity at constant volume C_v can be calculated from the heat capacity at atmospheric pressure C_p by using the known thermodynamic relation [21]:

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

where β is the thermal expansion coefficient. The data needed were taken from [14, 32, 34].

The translational heat capacity C_{tr} was calculated in the Debye approximation using the characteristic temperature Θ_D=64.6K obtained from expression $\Theta_D = \upsilon \left(\hbar/k_B\right) \left(6\pi^2 n\right)^{\frac{1}{3}}$ and it is close to $3R$ (Fig. 2). The contribution of intramolecular vibrations to the heat capacity C_{in} was calculated in the Einstein approximation using the intramolecular vibrational frequencies ν_i [35]. Rotational component C_{rot} was determined as C_{rot}=C_v-C_{tr}-C_{in}. All calculated contributions are shown in Fig. 2. It is seen that C_{rot} decreases with temperature increase, approaching to $3/2R$ at premelting temperature, which is characteristic for a free three-dimensional rotator.
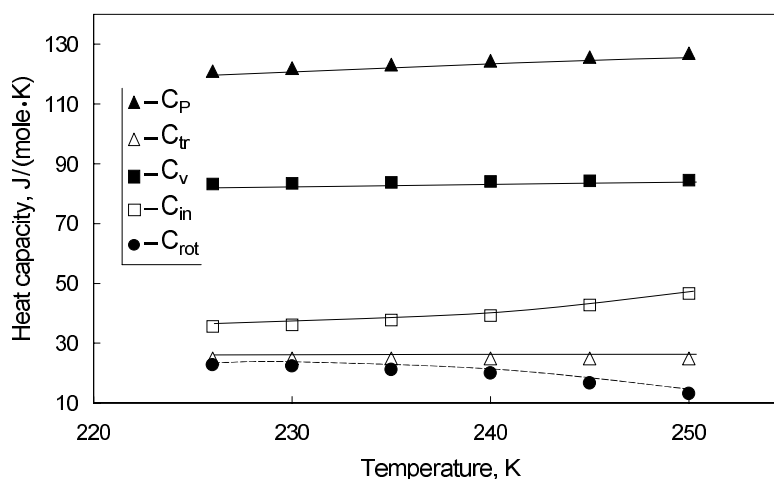

Fig. 2 Temperature dependences of the heat capacity contributions in solid CCl_4(Ib): C_p is the heat capacity at constant pressure [33], C_v is the heat capacity at V_{mol}=86.48 cm3/mole, C_{in}, C_{tr}, and C_{rot} are its intramolecular, translational, and rotational components, respectively.

To compare experimental results of thermal conductivity with theory correctly it is necessary to use data at constant density to exclude the effect of thermal expansion. The experimental data of the isochoric thermal conductivity of CCl_4(Ib) (V_{mol}=86.48 cm^3/mole) is shown in Fig. 3 according to [14] (black squares).

As the temperature increases, the isochoric thermal conductivity of CCl_4 also increases. The computer fitting of the thermal conductivity using equations (12, 13, 14, 15, 16) was performed by the least square method, varying the coefficients A, B, C, and α. The parameters of the Debye model used at the fitting (a [14], υ (Fig. 1)), and the fitted values A, B, C, α are listed in Table 1.

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

V_{mol}, cm^3/mole	a, 10^{-10}m	υ, m/s	γ	α	A, 10^{-16}s/K	B	C
86.48	5.34	1118	2.62	1.5	1.4	6.1	2.47

The results for fitting the isochoric thermal conductivity are shown in Fig. 3 (solid

line) along with the contributions (dashed lines) to the heat transfer from the low-frequency phonons Λ_{ph} and the high-frequency "diffusive" modes Λ_{dif}. The dotted line shows the lower limit of thermal conductivity Λ^*_{min} (19) calculated with the inclusion of the site to site rotational energy transfer. The dash-and-dot line is the lower limit of the thermal conductivity Λ_{min} (18) calculated according to Cahill and Pohl [28]. The vertical dash-and-dot line corresponds to the phase transition temperature T_f (II→Ib). The heat transfer by phonons Λ_{ph} initially decreases with increasing temperature, then passes through a smooth minimum and begins to increase The effect can be attributed to attenuation of phonon-rotation scattering, as we will discuss below. As temperature rises, the heat transfer by the "diffusive" modes increases. It can be noted in Fig. 3 that our theoretical calculations of thermal conductivity agree well with experimental data [14].
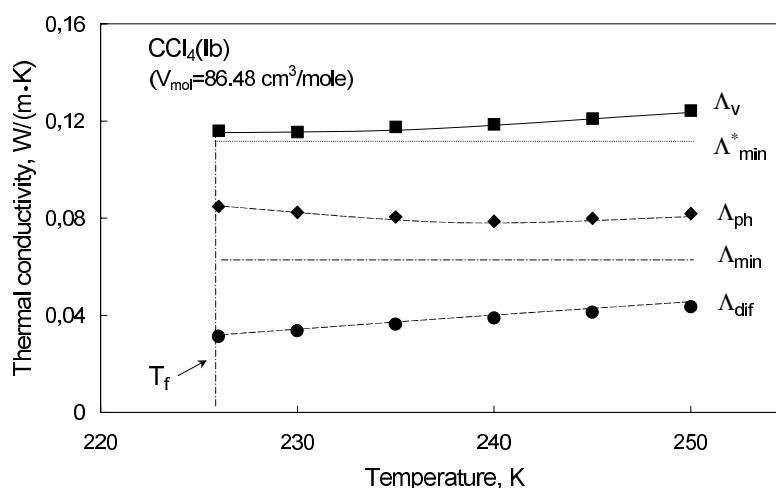

Fig. 3 Isochoric thermal conductivity Λ_v of solid CCl_4 (black squares) [14]. The solid line is the fitting curve to isochoric thermal conductivity. Λ_{ph} and Λ_{dif} are contributions of phonons and "diffusive" modes to heat transfer, respectively. The lower limits of the thermal conductivity Λ_{min} and Λ^*_{min} are calculated according to equations (18, 19).

It can also be seen in Fig. 3 that the isochoric thermal conductivity of solid CCl_4 is close to its lower limit Λ_{min}. This circumstance has at least two important consequences. Firstly, the proximity of the absolute value of the thermal conductivity to its lower limit gives us reason to expect that its temperature dependence is mainly determined by acoustical vibrations with relatively small wave vectors. Secondly, one expects substantial deviations from the law $\Lambda \propto 1/T$. This circumstance cannot, however, be account for the growth of the isochoric thermal conductivity in the OD phase of solid CCl_4. The discussion of the lower limit of thermal conductivity of molecular crystals brings up the inevitable question: should the site-to-site transport of the rotational energy of the molecules be taken into account? The minimal values of the experimental thermal conductivity Λ_v is 1.07 times higher than Λ^*_{min} calculated by equation (19), and 1.8 times higher than Λ_{min} calculated by equation (18). The above correlation between the Λ_{min} and Λ^*_{min} suggests the positive answer.

To answer questions as to basic peculiarities of phonon-rotational coupling in the OD phase of CCl_4, we have undertaken to separate the phonon-phonon and phonon-rotational contributions to the total thermal resistance. The additional phonon scattering (comparing to the phonon-phonon one) may originate in the orientationally disordered phases of molecular crystals due to the collective sort-range correlations of rotational motion of molecules.

We assume that the contributions of the different scattering mechanisms to the thermal resistance are additive [1]:

$$\sum_i W_i = W_{pp} + W_{pr1} + W_{pr2}, \tag{22}$$

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, 4, 5) we have:

$$W_{pp} = 2\pi^2 \upsilon AT \left/ k_B \int_0^{\omega_0} d\omega \right., \tag{23}$$

$$W_{pr1} = 2\pi^2 B^2 \Lambda_{rot} T \left/ k_B \upsilon^3 \rho \int_0^{\omega_0} d\omega \right., \tag{24}$$

$$W_{pr2} = 2\pi C^2 T^2 C_{rot} \left/ \left(\upsilon^6 \rho^2 \left| \int_0^{\omega_0} \frac{d\omega}{\omega^2} \right| \right) \right., \tag{25}$$

Figure 4 shows the calculated results for thermal resistance in OD phase of CCl_4. The total thermal resistance $W = 1/\Lambda_{ph}$ is shown with black squares. The solid curve is the sum of the thermal resistances, calculated by Eqs. (23, 24, 25). Phonon-phonon component of the thermal resistance W_{pp} increases slowly with temperature. The thermal resistance W_{pr1} due to the one-phonon scattering by rotational excitations of molecules is practically constant up to 240 K, and then decreases. The two-phonon component W_{pr2} of the total thermal resistance is practically zero (not exceeds $3 \cdot 10^{-5}$ m·K/W).

The decrease of the thermal resistance caused by one-phonon scattering, relative to the maximum is around 30 %. In the temperature range 226-240 K the additional contribution of W_{pr1} to the total thermal resistance is about 50 % of the phonon-phonon component and then decreases. The temperature dependence of the phonon-rotation thermal resistance of CCl_4(Ib) is similar to that observed for the β-phase of solid SF_6 above 160 K [5]. The observed effect, as in the case of solid SF_6, can be attributed to a weakening of the phonon scattering on collective rotational excitations of the CCl_4 molecules as the correlations of their rotation becomes weaker. This is in agreement with the data in [9–11], according to which the character of the molecular motion in the OD phase of CCl_4 is closely similar to that in the liquid state. Hence, it follows that the increase of the isochoric thermal conductivity in OD phase of CCl_4 can be attributed to the decrease in the contribution of phonon scattering by collective orientational excitations of molecules upon defreezing of their rotational motion.
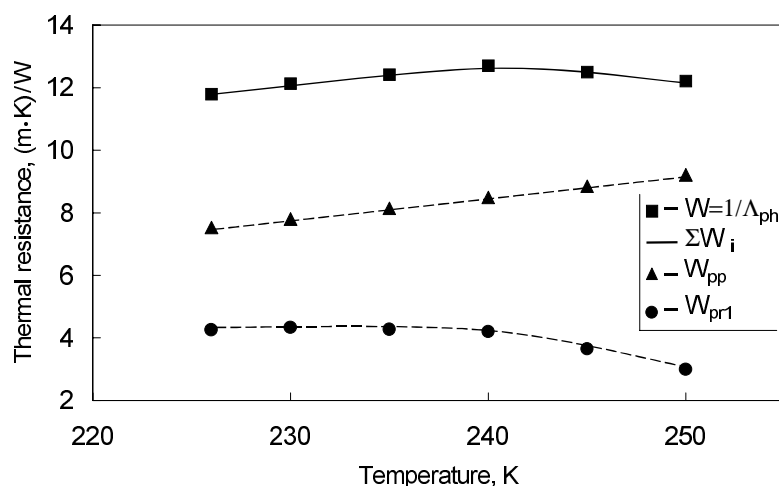
Fig. 4 Contributions of the phonon-phonon scattering W_{pp}, and one-phonon W_{pr1} mechanisms of scattering to the total thermal resistance of solid CCl_4. Square symbols indicate total thermal resistance $W=1/\Lambda_{ph}$. The solid line shows the sum of thermal resistances W_{pp}, W_{pr1}, and W_{pr2}.

5   Conclusions

It is shown that the isochoric thermal conductivity of CCl_4 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. The total thermal resistance in molecular crystals is determined by both phonon-phonon and phonon-rotation scattering mechanisms. The contributions of phonon-phonon, one-, and two-phonon scattering to the total thermal resistance of solid CCl_4 are calculated supposing additive contributions of the different scattering mechanisms. The increase of the isochoric thermal conductivity with increased temperature can be attributed to the decrease of the phonon scattering by the collective orientational excitations of the molecules as their rotational correlation motion is damped. It was found that the phonon-rotation and phonon-phonon scattering in solid $CCl_4(Ib)$ are close in their magnitudes. The main contribution to the phonon-rotation scattering gives one-phonon processes like in the case of CH_4 [22, 23].

Acknowledgment

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