Computational method for studying the thermal conductivity of molecular crystals in the course of condensed matter physics

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Abstract. This paper presents a computational method for studying the thermal conductivity of molecular crystals that can be used in the educational course of condensed matter physics. This method is based on the Debye model of thermal conductivity in the approximation of the corresponding relaxation times and allows studying the heat transfer processes features in simple molecular crystals at temperatures close to or above Debye temperature. The thermal conductivity is analysed in the framework of modified Debye model in which heat is transferred by low-frequency phonons and above the phonon mobility edge by “diffusive” modes migrating randomly from site to site. The mobility edge ω0 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 molecular crystals are calculated under the assumption that the different scattering mechanisms contribute additively. The presented computational method will be useful in pedagogical activities for teaching students of physical faculties.

1. Introduction

The current state of physical materials science is characterized by the search, creation, and comprehensive study of the new materials properties. Studies on condensed matter physics are the basis for the creation of new materials and structures with specified physical and mechanical properties. A promising direction of such research is molecular crystals in the properties of which the crystalline state features are most clearly manifested [13]. Thermophysical studies of molecular crystals carried out in the field of condensed matter physics have opened the way to their various practical applications. Molecular crystals can be used as refrigerants, which allow increasing the cold reserves in the cryostat. With space technologies development, the need arose for cooling equipment operating in zero gravity conditions, with that molecular crystals successfully cope. There is also considerable interest to molecular crystals in astrophysics since the giant planets consist mainly of crystallized gases. Molecular crystals are found in the atmospheres of many planets and comets nuclei, which allows by analyzing their emission and reflection spectra to solve the problem of studying the composition and properties of distant celestial bodies.

It should be noted that an important aspect of quality education is the constant introduction of the latest scientific advances in condensed matter physics into the educational process [28], which ensures
its innovation and compliance with the current stage of society development. In this paper we present an effective computational method that is used in research on the thermal conductivity of molecular crystals and can be used to teach students in the study of the course of condensed matter physics. One of the urgent and at the same time the most difficult problems in the condensed matter physics is the problem of studying the processes of energy transfer [36]. The transfer processes in dielectric crystals associated with such a kinetic phenomenon as thermal conductivity are of interest to researchers. Data on thermal conductivity allow us to obtain important information about the dynamics of the crystalline lattice. There are a number of mechanisms that determine the thermal conductivity, and a number of processes that limit the effectiveness of each of the mechanisms. The development of industrial technologies has contributed to the creation of high-precision methods for the study of thermal conductivity, which made it possible to obtain more complete information about the nature of the interaction in crystals. However, accurate, quantitative prediction of the amount of thermal conductivity due to the complexity of describing specific heat transfer mechanisms for real crystals is possible only in some cases [15].

Molecular crystals possess a number of peculiarities, which can significantly influence the dynamics of the crystalline lattice. The thermal and mechanical properties of simple molecular crystals are determined by both translational motion and orientational dynamics of molecules at sites of the crystalline lattice [29], [40]. 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 [20]. The peculiarities of translation-rotation coupling depend on molecular and crystal symmetry, and are determined by the relationship between central and non-central intermolecular interaction forces. At temperatures close to or above the Debye temperature (T≥ΘD), the general regularities of heat transfer in molecular crystals can be formulated as follows. A strong translational-orientational interactions contribute significantly to the thermal resistance W = 1/Λ [12], [20]. This, in turn, leads to large deviations of the isochoric thermal conductivity from the Λ ≈1/T law owing to its approach to a certain lower limit Λmin. 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 λ/2, and the site-to-site heat transport proceeds as a diffusive process [26]. In this case the lower limit of the lattice thermal conductivity Λmin can be written as [7]:

\[
Λ_{\text{min}} = \left( \frac{\pi}{6} \right)^{\frac{1}{3}} k_B n^{\frac{2}{3}} \sum_i \Theta_i \left( \frac{T}{\Theta_i} \right)^{2/3} \int_0^1 \frac{x^3 e^x}{(e^x - 1)^2} dx.
\]  

The summation is over three (one longitudinal and two transverse) sound modes with the sound velocities \( v_i \), \( \Theta_i \) is the Debye cutoff frequency for each polarization in Kelvins: \( \Theta_i = v_i (\hbar/k_B) (6\pi^2 n)^{1/3} \), \( n \) is the number of molecules per unit volume, and \( k_B \) is Boltzmann’s constant.

In molecular crystals with a relatively weak non-center interaction, the changeover from libration to weakly hindered rotation is observed with increasing temperature. In this case, the translational–orientational component of the thermal resistance is reduced and the isochoric thermal conductivity can increase with an increase in the temperature. A similar behavior has been observed in orientationally disordered phases of molecular crystals and in some special cases of the development of orientational mobility without subsequent phase transition [24], [25], [38], [39].

This article addresses the question of the application of the computational method by students for the practical study of the peculiarities of heat transfer processes in molecular crystals with different types of translation-rotation coupling.
2. Computational method

2.1. Modification of the Debye thermal conductivity model

The first stage of computational method is devoted to modification of the Debye thermal conductivity model to take into account the heat transfer by low-frequency phonons and “diffuse” modes. This calculation was performed on the basis of the Debye’s expression for thermal conductivity [15] using the approach of Roufosse and Klemens [43] who used the idea of a lower limit for the phonon mean-free path:

\[ \Lambda = \frac{k_B}{2\pi^2\nu^2} \int_0^{\omega_D} I(\omega)\omega^2 d\omega \]  

(2)

where \( \nu \) is the polarization-averaged sound velocity, \( \omega_D \) is the Debye frequency (\( \omega_D = (6\pi^2)^{\frac{1}{3}} \nu / a \)), \( I(\omega) \) is the phonon mean-free path, and \( a \) is the lattice constant. At \( T \geq \Theta_D \) the phonon-mean free path is restricted mainly by the \( U \)-processes and can be written as:

\[ I_u(\omega) = \frac{\nu}{AT \omega^2}, \]

(3)

\[ A = \left(18\pi^3/\sqrt{2}\right)k_B^2/ma^2\omega_D^3 \]

(4)

where the Grüneisen parameter \( \gamma = -\left(\partial \ln \Theta_D / \partial \ln V\right)_T \), \( I_u(\omega) \) is the phonon mean free path determined by \( U \)-processes, \( m \) is the average atomic (molecular) weight.

According to the model of the minimum thermal conductivity the mean free path \( I(\omega) \) of vibrational modes is described by equation (3) for frequencies smaller then \( \omega_0 \) otherwise it is a constant of the order of inter atomic distance [43]. In this case \( I(\omega) \) can be written as:

\[ I(\omega) = \begin{cases} \frac{\nu}{AT \omega^2}, & 0 \leq \omega \leq \omega_0, \\ \alpha \pi \nu / \omega = \alpha \lambda / 2, & \omega_0 < \omega \leq \omega_D \end{cases} \]

(5)

where \( \alpha \) is the numerical coefficient of the order of unity. The frequency \( \omega_0 \) can be found by substituting of \( I(\omega) \) in equation (5) at \( \omega = \omega_0 \):

\[ \frac{\nu}{AT \omega_0^2} = \frac{\alpha \pi \nu}{\omega_0}. \]

(6)

It is

\[ \omega_0 = 1/\alpha \pi AT. \]

(7)

The condition (6) 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 \( \omega_0 \) 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 [7]. If the mean free path of all modes exceeds \( \lambda / 2 \) the thermal conductivity is determined solely by the processes of phonon scattering. At \( \omega_0 \leq \omega_D \) the integral of thermal conductivity (2) is subdivided into two parts describing the contributions to the heat transfer from the low-frequency phonons \( \Lambda_{ph} \) and high-frequency "diffusive" modes \( \Lambda_{dif} \):

\[ \Lambda = \Lambda_{ph} + \Lambda_{dif}. \]

(8)
2.2. Accounting for translation-rotation coupling

The second stage of computational method is devoted to accounting translation-rotation interaction in the Debye model of thermal conductivity. The extra phonon scattering at librions leads to nothing but renormalization of the coefficient $A$ as compared to pure phonon-phonon scattering [29]. In orientationally disordered phases of molecular crystals there is no long-range order, which suggests that the distinct pure libration modes cannot propagate in the crystal. Nevertheless, the correlation effects are still strong immediately after the phase transition and the short-range orientational order persists. In this region there is strong phonon scattering at the short-range orientational order fluctuations and it becomes weaker on a further temperature rise (the free molecule rotation does not lead to phonon scattering) [20]. Therefore, we assumed that the heat transfer in molecular crystals at $T > T_D$ 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 [27], [48]. Using the equations for one- and two-phonon relaxation times [27], the phonon mean free path of one- and two-phonon scattering can be expressed as [38]:

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

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

where $l_I(\omega)$ and $l_{II}(\omega)$ are the phonon mean free paths for one and two-phonon scattering, respectively, $B$ and $C$ are the constants of non-central intermolecular interactions, $\Lambda_{\text{rot}}$ is the thermal conductivity of the orientational subsystem, $C_{\text{rot}}$ is the rotational heat capacity per unit volume. In the first approximation $B = C^2$ [27].

The coefficient $B$ can be found from the pressure dependence of orientational ordering temperature:

$$B = -\left(1 / \chi_T \right) \left(\partial \ln T_r / \partial P \right)$$

where $\chi_T$ is the isothermal compressibility, $T_r$ is temperature of the orientational phase transition, $P$ is the pressure. The thermal conductivity $\Lambda_{\text{rot}}$ can be found from the well-known gas-kinetic expression:

$$\Lambda_{\text{rot}} = \frac{1}{3} C_{\text{rot}} a^2 \tau^{-1}$$

where $\tau$ is the characteristic time of orientational excitation transfer from one lattice site to another. This time can be estimated from relation $\tau \approx \hbar / \Delta E$ [6], where the non-central part $\Delta E$ of the intermolecular interaction was calculated on the basis of the expression given in [48] relating it to the temperature of transition into the orientationally ordered phase of corresponding molecular crystals.

Then, $l(\omega)$, the combined phonon mean-free path, can be written as:

$$l(\omega) = \sum l_i(\omega) = \sum \left(\int l_i(\omega) \right)^{-1}.$$  

By substituting (3, 9, 10) in (13), the combined phonon mean-free path can be expressed as [38]:

$$l(\omega) = \left( \frac{AT \omega^2}{\rho v^3} + \frac{B^2 \Lambda_{\text{rot}} \omega^2}{\rho v^3} + \frac{C^2 k_B C_{\text{rot}} T^2 \omega^4}{\pi \rho v^8} \right)^{-1}.$$  

Expression (14) is not applicable if $l(\omega)$ becomes of order 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 [26]. Let us assume that in the general case:
\[ l(\omega) = \begin{cases} l_2(\omega), & 0 \leq \omega \leq \omega_b, \\ \alpha \pi \nu / \omega = \alpha \lambda / 2, & \omega_b < \omega \leq \omega_D \end{cases} \]  

(15)

where \( \alpha \) is the numerical coefficient of the order of unity. The frequency \( \omega_0 \) can be found from the condition:

\[
\left( \frac{AT\omega_0^2}{\nu} + \frac{B^2 \Lambda_{\text{rot}} T \omega_0^2}{\rho \nu^5} + \frac{C^2 \kappa B C_{\text{rot}} T^2 \omega_0^4}{\pi \rho^2 \nu^8} \right)^{-1} = \frac{\alpha \pi \nu}{\omega_0}.
\]  

(16)

It equals

\[
\omega_0 = -u\sqrt{-\eta + \sqrt{u^2 + \eta^2}} \sqrt{\omega_D - \omega_0^2} + \left( -\eta + \sqrt{u^2 + \eta^2} \right) \sqrt{\omega_D - \omega_0^2} \right)^{1/2}
\]  

(17)

where the parameters \( u \) and \( \eta \) are:

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

(18)

The integral of thermal conductivity splits into two parts describing the contributions to the thermal conductivity from the low-frequency phonon and the high-frequency “diffusive” modes. In the high-temperature limit \((T \gtrsim T_0)\) these contributions are:

\[
\Lambda_{\text{ph}} = \frac{k_B}{2\pi^2 \nu^7} \int_0^{\omega_0} \frac{\omega d\omega}{C^2 \kappa B C_{\text{rot}} T^2 \omega_0^3 + \frac{A T \omega_0}{\nu} + \frac{B^2 \Lambda_{\text{rot}} T \omega_0}{\rho \nu^5}}
\]  

(19)

\[
\Lambda_{\text{dif}} = \frac{\alpha k_B}{4\pi \nu} \left( \omega_D^2 - \omega_0^2 \right).
\]  

(20)

In the case of orientationally ordered phases equation (19) gives the well-known dependence \( \Lambda \propto 1/T \) at \( \omega_0 > \omega_D \)

\[
\Lambda_{\text{ph}} = \frac{k_B \omega_0}{2\pi^2 \nu^7 AT}.
\]  

(21)

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 \[31, 32, 33]. 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.

2.3. Phonon scattering

To answer questions as to basic peculiarities of phonon-phonon and phonon-rotational scattering of simple molecular crystals in the framework of third stage of this method 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 $W=1/\Lambda$ [29]. 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 [20], [39]. We assume that the contributions of different scattering mechanisms to the thermal resistance are additive [38]:

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

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 (2) and (3, 9, 10) we have:

$$W_{pp} = 2\pi^2 v AT / k_B \int_0^{\alpha_1} d\omega,$$

$$W_{pr1} = 2\pi^2 B^2 \Lambda_{nn} T / k_B \int_0^{\alpha_2} d\omega,$$

$$W_{pr2} = 2\pi C^2 T^2 C_{rot} / \left(\mu^2 \rho \int_0^{\alpha_3} \frac{d\omega}{\omega^2}\right).$$

3. The objects

Solid SF$_6$, CCl$_4$, and C$_6$H$_6$ crystals with different type of molecular rotational motion were chosen as an example to study of heat transfer processes features in the high-temperature phases of molecular crystals. The existence region of high-temperature $\beta$-phase of solid SF6 is extraordinarily large: the crystallization of SF6 occurs at 222.4 K, and the phase transition lowering the symmetry of the translational and orientational subsystems of the crystal does not occur until 94.3 K [16]. Sulphur hexafluoride is often classed as a substance that has a plastic crystalline phase. Indeed, the relative molar entropy of melting $\Delta S_m/R$ of SF$_6$ is 2.61 [47], which is close to Timmerman’s criterion. Here $R$ is the universal gas constant. However, the nature of orientational disorder in the high-temperature phase of SF$_6$ is somewhat different from that of plastic phases in other molecular crystals, where the symmetries of the molecule and its surroundings do not coincide. The SF$_6$ molecule has the octahedral symmetry. At 222.4 K sulphur hexafluoride crystallizes into $bcc$ lattice of $I_m3m$ ($O_h$) symmetry with two molecules per unit cell. As a result, the molecule and its surroundings have the same symmetry. On further cooling to 94.3 K, a polymorphous transition occurs, which suppresses the symmetry of the translational and orientational subsystem to the monoclinic one, of space group $C2/m$ ($C_{2h}$). The interaction between the nearest neighbors in the $bcc$ phase is favorable for molecular ordering caused by the S-F bonds along the $\{100\}$ direction and the interaction with the next nearest neighbors is dominated by repulsion between the F atoms. According to x-ray and neutron diffraction data [10], [11], [16], a strict order is observed in $\beta$-SF$_6$ just above the phase transition point. The structural dynamical factor $\Phi$ characterizing the degree of the orientational order is close to unity in the interval 95-130K. This feature distinguishes SF$_6$ from other plastic crystals, such as methane, carbon tetrachloride, adamantane and so on, where the long-range orientational order becomes disturbed immediately after the phase transition. Orientation disordering in SF$_6$ starts to intensify only above 140 K. As follows from the analysis of the terms of the Debye-Waller factor derived from neutron-
diffraeometric data for the β-phase of SF₆, the F atoms have large effective librational amplitudes. As temperature rises, the librational amplitudes increase to 20° and higher, but the F localization is still appreciable near the {100} direction. This implies that the orientational structure of SF₆ does not become completely disordered even at rather high temperatures. The disordering itself is dynamic by nature. The increasing amplitudes of librations are not the only factor responsible for the increasing orientational disordering with dynamic reorientations, which become more intensive due to frustrations of the intermolecular interactions [10], [11], [16], [17].

Carbon tetrachloride has an interesting feature: on cooling to 250.3 K liquid CCl₄ crystallizes into a face-centred cubic (fcc) form (I₄) with four molecules per unit cell, which at further temperature decrease by some degrees transforms into the rhombohedral phase (I₆) with 21 molecules per unit cell [37], [44]. Below 225.5 K the rhombohedral phase transforms into a monoclinic one of space symmetry group C2/c (C₂h) with Z=32. On heating, the low-temperature phase (II) always changes to the rhombohedral form. Because of low entropy of melting ΔS/R=1.21, the phase (I₄) of CCl₄ may be classified as “plastic” [46]. The three forms of solid CCl₄ 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, the molecular orientations in the phase (II) correlate closely with the directions of the highest-density distributions function in the phase (I). According to experimental data, the character of the molecular motion in the plastic phase of CCl₄ is closely similar to that in the liquid state. For example, for CCl₄ no discontinuities are observed in the curve of spin-spin relaxation time T₂ of ³⁵Cl on plastic phase melting [34] and in the curve of reorientational correlation time obtained from Raman line broadening [4], [9]. Zuk, Kieffe, and Clouter estimated the elastic constants of CCl₄ in the phase (I) by the Brillouin scattering method [49]. They discovered 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.

Solid benzene under the pressure of its own saturated vapor has only one crystallographic modification: it has the orthorhombic spatial symmetry Pnca (D_{2h}^{15}) with four molecules per unit cell [2], [8]. Benzene melts at 278.5 K and the melting-caused change in the entropy is ΔS/R=4.22 [47], 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 C₆H₆ is 120 K [18]. In the interval 90-120 K the second NMR moment of C₆H₆ drops considerably as a result of the molecule reorientations in the plane of the ring around the sixfold axis [1]. 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 10⁴ s⁻¹. On a further rise of the temperature it increases considerably, reaching 10¹¹ s⁻¹ near melting temperature. The basic frequency of the benzene molecule oscillations about the sixfold axis at 273 K is 1.05·10¹² s⁻¹ [40].

4. Results and discussion

To compare computational results obtained in the framework of above mentioned method with experimental results it is necessary to use the reliable experimental data on thermal conductivity of molecular crystals. Up to now, the thermal conductivity of solid SF₆ has been studied for several isochores in the narrow temperature interval near the melting point [22] and in the whole region of the existence of β-phase under isobaric conditions [39]. The thermal conductivity of solid CCl₄ had been measured at constant pressure in the temperature range 80-250 K [41] and on several isochores above 200 K [21]. At present, the thermal conductivity of solid C₆H₆ has been experimentally studied in the temperature range from 80 K to the melting temperature [23]. The isobaric thermal conductivity of solid C₆H₆ was also measured under the pressure above 100 MPa [42]. The experimental data of the isochoric thermal conductivity of solid SF₆ (V_{mol}=58.25 cm³/mole), CCl₄ (V_{mol}=86.48 cm³/mole) and C₆H₆ (V_{mol}=70.50 cm³/mole) [21], [23], [39] are presented in figure 1 as black squares. The computer simulation of the thermal conductivity of solid SF₆, CCl₄ and C₆H₆ using equations (16)-(20) was performed by the parameter fitting method [35], varying the coefficients A, B, C, and α.
Figure 1. Isochoric thermal conductivity $\Lambda_v$ of solid $\beta$-SF$_6$, CCl$_4$ (I$_b$), and C$_6$H$_6$. The solid line is the fitting curve for isochoric thermal conductivity. $\Lambda_{ph}$ and $\Lambda_{df}$ are contributions of phonons and “diffusive” modes to heat transfer, respectively. The lower limits of the thermal conductivity $\Lambda_{min}$ calculated according to equation (1). $T_f$ is the phase transition temperature.

The necessary for simulation data on sound velocity and density in solid $\beta$-SF$_6$, CCl$_4$ (I$_b$) and C$_6$H$_6$ were taken from [14], [38], [39]. To determine rotational components of the heat capacity of solid $\beta$-SF$_6$, CCl$_4$ (I$_b$) and C$_6$H$_6$, we used the method described in [16] and data cited in [3], [5], [16], [18], [30], [38], [39], [45]. The computer simulation results for isochoric thermal conductivity $\Lambda_v$ of solid SF$_6$, CCl$_4$ and C$_6$H$_6$ are shown in figure 1. As shown in figure 1, the simulation results for isochoric thermal conductivity of solid SF$_6$, CCl$_4$ and C$_6$H$_6$ (solid line) are in good agreements with experimental data and the maximum differences do not exceed 5%. The same figure shows the
contributions (dot-and-dash lines) to the heat transfer from the low-frequency phonons $\Lambda_{\text{ph}}$ and the high-frequency “diffusive” modes $\Lambda_{\text{dif}}$ (calculated by equations (19), (20)). The dotted lines in figure 1 illustrate the lower limit of the thermal conductivity $\Lambda_{\text{min}}$ (1) calculated for the isochoric case, according to Cahill and Pohl [7] in the framework of the Einstein model for the diffusive transfer of heat directly from site to site on a time scale of one-half of the period of oscillation. The parameters of the Debye model for thermal conductivity used in the simulation ($a, v, \gamma$), and the fitted values $A, B, C,$ and $\alpha$ 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 for computer simulation.

| Substance | $V_{\text{mol}}$, cm$^3$/mole | $a$, $10^4$cm | $v$, cm/s | $\gamma$ | $\alpha$ | $\Lambda$, $10^{17}$s/K | B | C |
|-----------|-----------------|--------------|---------|---------|--------|-----------------|---|---|
| $\beta$-SF$_6$ | 58.25 | 4.6 | 994 | 2.01 | 2.0 | 9.65 | 7.0 | 2.62 |
| CCl$_4$ ($I_b$) | 86.48 | 5.3 | 1118 | 2.62 | 1.5 | 13.9 | 6.1 | 2.46 |
| C$_6$H$_6$ | 70.50 | 4.9 | 2275 | 3.30 | 4.4 | 7.60 | 6.8 | 2.59 |

From figure 1, it can be noted that the experimental thermal conductivity $\Lambda_{\text{exp}}$ (black squares) at premelting temperatures approaches to its lower limit. As the temperature increases, the isochoric thermal conductivity in $\beta$-phase of solid SF$_6$ and in phase $I_b$ of solid CCl$_4$ also increases. At the same time, the isochoric thermal conductivity of solid C$_6$H$_6$ decreases with increasing temperature. It can also be seen from figure 1 that in OD phases of $\beta$-SF$_6$ and CCl$_4$($I_b$) heat is transferred by both phonons and “diffusive” modes, whereas in C$_6$H$_6$ above 150 K heat is basically transferred by “diffusive” modes. In $\beta$-phase of solid $\beta$-SF$_6$ heat transfer by phonons $\Lambda_{\text{ph}}$ decreases with temperature, passes through a minimum and then starts to grow. The observed effect can be attributed to a weakening of phonons scattering by collective rotational excitations of molecules as the correlations of their rotation becomes weaker. These findings are in good agreement with results of different structural study of solid SF$_6$ [11], [16], [17] according to which in solid SF$_6$ the nature of orientational disorder in the high-temperature $\beta$-phase of solid SF$_6$ is somewhat different from that of plastic phases in other molecular crystals, where the symmetries of the molecule and its surroundings do not coincide. As indicated in [16], in the $\beta$-phase of solid SF$_6$ observed a rather strict orientational order immediately after the phase transition at 93.4 K and intense growth of the orientational disordering processes starts only at temperature above 140 K that correlated well with simulation results for $\Lambda_{\text{ph}}$ presented in figure 1a. The Brillouin scattering results [19] also attest to a weaker translational-rotational coupling in the $\beta$-phase of solid SF$_6$.

In phase $I_b$ of crystalline CCl$_4$, the contributions of $\Lambda_{\text{dif}}$ increases and that of the $\Lambda_{\text{ph}}$ weakly decreases (figure 1b) this also can be attributed to the weakening of phonon scattering by rotational excitation of molecules. This again is in good agreement with results of structural study of solid CCl$_4$ cited in [4], [9], [34], [46]. Unlike $\beta$-phase of solid SF$_6$ in crystalline CCl$_4$($I_b$), the orientational disordering processes starts immediately after the phase transition to phase $I_b$ (225.5 K). According to results of experimental research [4], [9], [34], the character of the molecular rotational motion in the plastic phase of CCl$_4$ is closely similar to that in the liquid state i.e. nearly free rotation. Therefore, the temperature dependence of the $\Lambda_{\text{ph}}$ in phase $I_b$ of solid CCl$_4$ practically does not change with temperature at isochoric condition.

Theoretical models of heat transfer in solid dielectrics have predicted the thermal conductivity behaviour $\Lambda \propto 1/T$ at temperatures $T \geq \Theta_D$ [15]. The behaviour of temperature dependence of isochoric thermal conductivity $\Lambda_v$ of solid C$_6$H$_6$ is inconsistent with the theoretical prediction. Above 180 K, $\Lambda_v$ is practically constant and even starts to grow slightly at premelting temperatures. With temperature rises (figure 1c), the part of heat transferred by the “diffusive” modes $\Lambda_{\text{dif}}$ increases, and in a range of 110 K it becomes equal to the heat transferred by the low-frequency phonons $\Lambda_{\text{ph}}$. It is seen that our simulation results for thermal conductivity of solid C$_6$H$_6$ in good agreement with...
experimental data (black squares) cited in [23] if the different density of the samples is taken into account.

**Figure 2.** Temperature dependence of the phonon mobility edge $\omega_0$ for solid SF$_6$, CCl$_4$ and C$_6$H$_6$. $\omega_D$ is the Debye frequency.

The phonon mobility edge $\omega_0$ for solid SF$_6$, CCl$_4$ and C$_6$H$_6$ calculated by equations (17) and (18) are presented in figure 2. Phonon mobility edge temperature dependence in $\beta$-phase of solid SF$_6$ decreases with increasing temperature then passes through a minimum, and starts to increase. This increase can be related to decreasing of the phonon scattering, which occurs as the rotational correlations between the neighbouring molecules become weaker. In solid CCl$_4$ and C$_6$H$_6$, as the
temperature rises the phonon mobility edge $\omega_0$ decreases. This occurs because the nature of molecular rotational motion in these crystals practically does not change with temperature.

![Graphs showing thermal resistance vs temperature for β-SF$_6$, CCl$_4$, and C$_6$H$_6$.]

**Figure 3.** Contributions of the phonon–phonon scattering $W_{pp}$, and one-phonon $W_{pr1}$ scattering by collective rotational excitation to the total thermal resistance $W$ of solid β-SF$_6$, CCl$_4$ (I$_b$), and C$_6$H$_6$.

To study peculiarity of heat transfer processes in solid SF$_6$, CCl$_4$ and C$_6$H$_6$ we used above described computational method to separate the phonon-phonon and phonon-rotational contributions to the total thermal resistance. Figure 3 shows the obtained results for thermal resistance. The total thermal resistance was determined as $W = 1/\Lambda_{ph}$. The solid curve is the sum of the thermal resistances,
calculated by equations (23)-(25). The solid line shows the sum of thermal resistances \(W_{pp}, W_{pr1},\) and \(W_{pr2}\). Square symbols indicate total thermal resistance \(W=1/\Lambda_{pp}\). The two-phonon component \(W_{pr2}\) of the total thermal resistance are practically zero in all cases (not exceeds \(4\cdot10^{2}\) m-K/W). The contributions of phonon–phonon scattering \(W_{pp}\) and one-phonon scattering by rotational excitations of molecules \(W_{pr1}\) are presented in figure 3 as dashed lines. For investigated molecular crystals the phonon–phonon component \(W_{pp}\) of the total thermal resistance increases with temperature. The behaviour of temperature dependences of the phonon-rotational thermal resistance \(W_{pr1}\) are differs. The observed variations in temperature dependences of the phonon-rotational thermal resistance \(W_{pr1}\) of solid SF\(_6\), CCl\(_4\) and C\(_6\)H\(_6\) can be explained by the different type of rotational motion of molecules in these crystals.

5. Conclusion

The results obtained by applying the computational method clearly demonstrate the features of heat transfer processes in molecular crystals with different types of translation-orientation interaction. The experimental temperature dependence of isochoric thermal conductivity for simple molecular crystals can be adequately described by Debye approximation in the frame of the model where heat is transferred by phonons and “diffusive” modes on the assumption that the mean free path of phonons cannot be smaller than half the wavelength. Unlike the classical Debye model of thermal conductivity described method makes it possible to take into account not only the heat transfer by low-frequency phonons and “diffusive” modes but also the influence of translation-rotation coupling on the heat transfer processes. The presented computation method based on the modified Debye model of thermal conductivity can be used in the educational process within the teaching the discipline “Condensed matter physics”, in particular, in the framework of a lecture on the topic “Thermal properties of dielectrics”. In this method, students studying different molecular crystals can track how the structure of the molecules, the types of interaction, the structure of the translation and orientation subsystems and their dynamics affect the thermal conductivity of molecular crystals.

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