

TEMPERATURE AND VOLUME DEPENDENCE OF THERMAL CONDUCTIVITY IN SOLID CHCl_3

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Abstract

The temperature and volume dependences of the thermal conductivity of solid CHCl_3 are described in the framework of 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 mobility edge ω_o is determined from the condition, that the phonon mean free path restricted by the Umklapp processes cannot become smaller than half the phonon wavelength. Significant deviations from the dependence $\Lambda \propto 1/T$ are explained by the thermal conductivity approaching its lower limit.

1. Introduction

Heat transfer in a dielectric solid, where the electrons are tightly bound to the atomic nuclei, is realized through the transfer of phonons, quanta of energy associated with lattice vibrations. At low temperatures, well below the Debye temperature of solids (Θ_D), heat transport in simple molecular crystals is adequately described by mainly of basic theoretical models [1]. In the high temperature region ($T \geq \Theta_D$), however, the 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 the thermal conductivity should be inversely proportional to temperature ($\Lambda \propto 1/T$), whereas the experimental investigations of the thermal conductivity of molecular crystals show considerable deviations from the above dependence [2]. Essentially all basic concepts of heat transfer were created mainly on the basis of studies of the simplest crystalline structure, namely atomic crystals. Therefore, the features typical for molecular crystals were not taken into account in them. One of these features that can affect the temperature dependence of thermal conductivity is the translation-rotation coupling. In the context of the present study we want to emphasize that the additional factor which can determine the temperature dependence of thermal conductivity is also the approaching of the thermal conductivity to its lower limit.

The purpose of this paper was to study basic features of heat transfer in the orientationally ordered phase of molecular crystals. Our previous measurements have revealed a considerable deviation of the isochoric thermal conductivity of solid CHCl_3 from the dependence $1/T$ [2]. The effect was explained qualitatively but we did not provide a quantitative interpretation. The present work continues investigation of the observed effect on solid CHCl_3 . The purpose of this study is to analyse temperature dependence of the isochoric thermal conduc-

tivity of CHCl_3 by using the model, which assumed that the heat is transferred by low-frequency phonons and above the mobility edge by “diffusive” modes.

2. The object

Solid chloroform (CHCl_3) under the pressure of its own saturated vapor, has only one crystallographic modification: it has the spatial symmetry $P_{nma} \left(P_{2h}^{16} \right)$ with four differently oriented molecules in the orthorhombic cell [3,4]. It is known from Raman and IR absorption (20 K) data [4] that the translational modes take the frequency band up to 60 cm^{-1} (86 K) and partially overlap with the librational modes in the $60\text{-}100 \text{ cm}^{-1}$ band (86-144 K). Nuclear quadrupole resonance on the ^{35}Cl nuclei has been observed in CHCl_3 up to the melting temperature $T_m=209.7 \text{ K}$ [5]. These data indicate that there are no molecular reorientations at frequencies above 10^4 s^{-1} . The melting-caused change in the entropy $\Delta S_f/R=5.4$ (Timmermans criterion), also attempts to a high degree of ordering in CHCl_3 [6]. At present, the thermal conductivity of solid CHCl_3 has been experimentally studied by the linear-flow method under saturated vapor pressure in the temperature range from 80 K to the melting temperature [2] and the isochoric thermal conductivity has been directly investigated at premelting temperatures [7].

3. Model

The calculation was performed on the basis of the Debye's expression for thermal conductivity [1] using the approach of Roufosse and Klemens [8] who used the idea of a lower limit for the phonon mean free path:

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

where ω_D is the Debye frequency ($\omega_D = (6\pi^2)^{1/3} \nu / a$, a is the lattice parameter), $l(\omega)$ is the phonon mean free path, ν is the polarization-averaged sound velocity and ω is the angular frequency. At $T \geq \Theta_D$ the phonon mean free path is mainly determined by the U -processes and for perfect crystal can be written as:

$$l_u(\omega) = \nu / A T \omega^2, \quad (2)$$

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

where the Grüneisen parameter $\gamma = -(\partial \ln \Theta_D / \partial \ln V)_T$, m is the average atomic (molecular) weight.

Expression (2) is not applicable if $l(\omega)$ becomes of order or smaller than half the phonon wavelength $\lambda / 2 = \pi \nu / \omega$. A similar situation was considered previously only for the case of U -processes [8]. Let us assume that in the general case:

$$l(\omega) = \begin{cases} \nu / A \omega^2 T & 0 \leq \omega \leq \omega_0, \\ \alpha \pi \nu / \omega = \alpha \lambda / 2, & \omega_0 < \omega \leq \omega_D, \end{cases} \quad (4)$$

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

$$\frac{\nu}{AT\omega_0^2} = \frac{\alpha\pi\nu}{\omega_0}, \quad (5)$$

It equals to

$$\omega_0 = 1/\alpha\pi AT, \quad (6)$$

Condition (5) is the well-known Ioffe-Regel criterion, which implies localization. We can therefore assume that the excitations with frequencies 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 [9].

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:

$$\Lambda = \Lambda_{\text{ph}} + \Lambda_{\text{dif}}, \quad (7)$$

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

$$\Lambda_{\text{ph}} = \frac{k_B \omega_0}{2\pi^2 \nu AT}, \quad (8)$$

$$\Lambda_{\text{dif}} = \frac{\alpha k_B}{4\pi\nu} (\omega_D^2 - \omega_0^2), \quad (9)$$

4. Results and discussion

As was marked above, at temperature close to or above the Debye temperature ($T \geq \Theta_D$) the thermal conductivity of perfect crystals is determined solely by phonon-phonon scattering and it is expected to follow the law $\Lambda \propto 1/T$ [1]. In order to obey the law, the volume of the crystals should remain invariable, because the modes would otherwise change and so would the temperature dependence of the thermal conductivity [10,11]. Therefore, in order to find the correlation between experimental results for thermal conductivity and theoretical prediction it is necessary to compare the data at constant density to exclude the influence of thermal expansion.

Nevertheless, isochoric studies of the thermal conductivity of molecular crystals [2, 12-15] show a considerable deviation from this law. These discrepancies may be due to the approach of the thermal conductivity to 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 they cannot become smaller than half the phonon wavelength $\lambda/2$ and the site-to-site heat transport proceeds as a diffusive process. In this case the lower limit of the lattice thermal conductivity Λ_{min} at $T \geq \Theta_D$ can be written as [9]:

$$\Lambda_{\text{min}} = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \nu \left(\frac{T}{\Theta_D}\right)^2 \int_0^{\Theta_D/T} \frac{x^3 e^x}{(e^x - 1)^2} dx, \quad (10)$$

where $\Theta_D = \nu(\hbar/k_B)(6\pi^2 n)^{1/3}$, n is the number of atoms (molecules) per unit volume and k_B is the Boltzmann constant. The calculated values of Λ_{min} were as a rule considerably smaller than experimental ones [2,12,13]. 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, their heat capacity is saturated in proportion to the total molecular degrees of freedom. Taking into account this feature of molecular crystals, lower limit of the thermal conductivity can be represented as [12]:

$$\Lambda_{\min}^* = \frac{1}{2} \left(\frac{\pi}{6} \right)^{1/3} \left(1 + \frac{z}{3} \right) k_B n^{2/3} (\nu_\ell + 2\nu_t), \quad (11)$$

where ν_ℓ and ν_t are the longitudinal and transversal sound velocities respectively, z is the number of rotational degrees of freedom. To our knowledge, no information at all is available on the velocity of sound in solid CHCl_3 . In this respect, the phonon velocity (Table 1) was calculated by the method described in [16]. The necessary initial data were taken from [3-6]. Determining the Debye temperature (86 K) we made use of the boundary frequency of translational modes from the Raman and IR absorption data [4] at 20 K.

Table 1. Parameters of the Debye model for thermal conductivity used in the fitting, calculated g_{th} and experimental g_{exp} Bridgman coefficients and other quantities which were used for calculation.

$V_{\text{mol}},$ cm^3/mole	$a,$ 10^{-10} m	$\nu,$ m/s	α	$A,$ 10^{-16} s/K	g_{exp}	g_{th}
59.5	4.72	1310	2.48	1.24	3.9	2.9

Our earlier researches of thermal conductivity for solid CHCl_3 which have been carried out in [2], are shown in Fig.1 (black squares). The values of isochoric thermal conductivity Λ_v correspond to the constant volume $V_{\text{mol}}=59.5 \text{ cm}^3/\text{mole}$ [2], occupied by the samples at the temperature of growing ($T=80\text{K}$). As the temperature increases, the isochoric thermal conductivity of solid CHCl_3 decreases according to the dependence $\Lambda_v \propto T^{-0.8}$ (Fig. 1). The computer fitting of the thermal conductivity using Eqs. (7-9) was performed by the least square method, varying the coefficients A and α . The parameters of the Debye model for thermal conductivity used in the fitting (a , ν), and the fitted values A and α are listed in Table 1 along with the Bridgman coefficients obtained in the experiment [7] and calculated within this model.

The fitting results for isochoric thermal conductivity are shown in Fig. 1 (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 Eqs. (8), (9)). The dotted line shows the lower limit of thermal conductivity $\Lambda_{\min}^*$ (11) 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 the thermal conductivity $\Lambda_{\min}$ (10) calculated according to Cahill and Pohl in the framework of the Einstein model for the diffusive transfer of heat directly from atom to atom [9].

It is seen (Fig.1) that the “diffusive” behaviour of the oscillatory modes appears above 100K. As temperature rises, the amount of heat transferred by the “diffusive” modes increases and at 165K it becomes equal to the heat transferred by the low-frequency phonons. Above 180K most of the heat is transported by the “diffusive” modes. The minimal values of thermal conductivity Λ_v (Fig.1) are 1.3 times higher than $\Lambda_{\min}^*$ calculated by Eq. (11) and 2.7 times higher than $\Lambda_{\min}$ calculated by Eq. (10). 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 above correlation between the $\Lambda_{\min}$ and $\Lambda_{\min}^*$ suggests the positive answer.

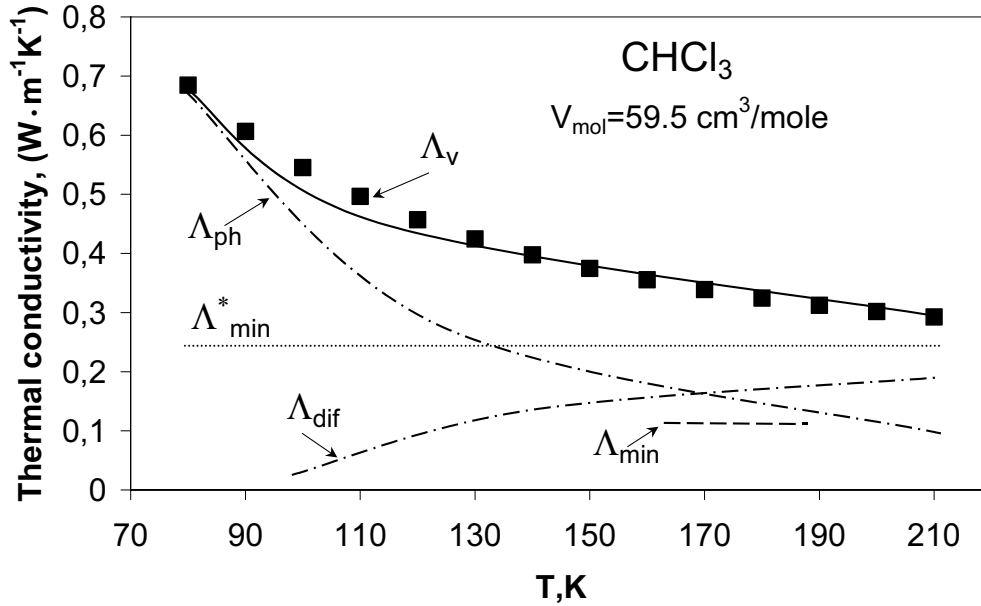


Fig.1. Isochoric thermal conductivity Λ_v of solid CHCl_3 (squares)[2]. The solid line is the fitting curve for isochoric thermal conductivity. Λ_{ph} and Λ_{dif} are contributions of phonons and “diffusive” modes to heat transfer, respectively. The lower limits of the thermal conductivity $\Lambda_{\min}$ and $\Lambda_{\min}^*$ calculated according to Eqs. (10), (11), respectively.

The dependence of the thermal conductivity on the molar volume can also be interpreted within this model. The volume dependence of the thermal conductivity is characterized by the Bridgman coefficient [10,11]:

$$g = - \left(\frac{\partial \ln \Lambda}{\partial \ln V} \right)_T, \quad (12)$$

Using Eqs. (3), (7) and taking into account that $(\partial \ln A / \partial \ln V)_T = 3\gamma + 2q - 2/3$, where $q = (\partial \ln \gamma / \partial \ln V)_T$, we have:

$$g = \frac{\Lambda_{\text{ph}}}{\Lambda} g_{\text{ph}} + \frac{\Lambda_{\text{dif}}}{\Lambda} g_{\text{dif}}, \quad (13)$$

where

$$g_{\text{ph}} = - \left(\frac{\partial \ln \Lambda_{\text{ph}}}{\partial \ln V} \right)_T = 5\gamma + 4q - 1, \quad (14)$$

$$g_{\text{dif}} = - \left(\frac{\partial \ln \Lambda_{\text{dif}}}{\partial \ln V} \right)_T = -\gamma + \frac{1}{3} + \frac{2}{\omega_D^2 - \omega_0^2} (\omega_D^2 \gamma - \omega_0^2 \gamma_0), \quad (15)$$

$$\gamma_0 = 3\gamma + 2q - 1/3, \quad (16)$$

As seen in Table 1, the experimental [7] and calculated (13) Bridgman coefficients are in fairly good agreement if one notes that the value of g_{th} is estimated with large uncertainty

and the model disregards phonon dispersion and the real density of states. The temperature dependence of the Bridgman coefficient of solid CHCl_3 calculated by Eqs. (13-16) is depicted in Fig.2.

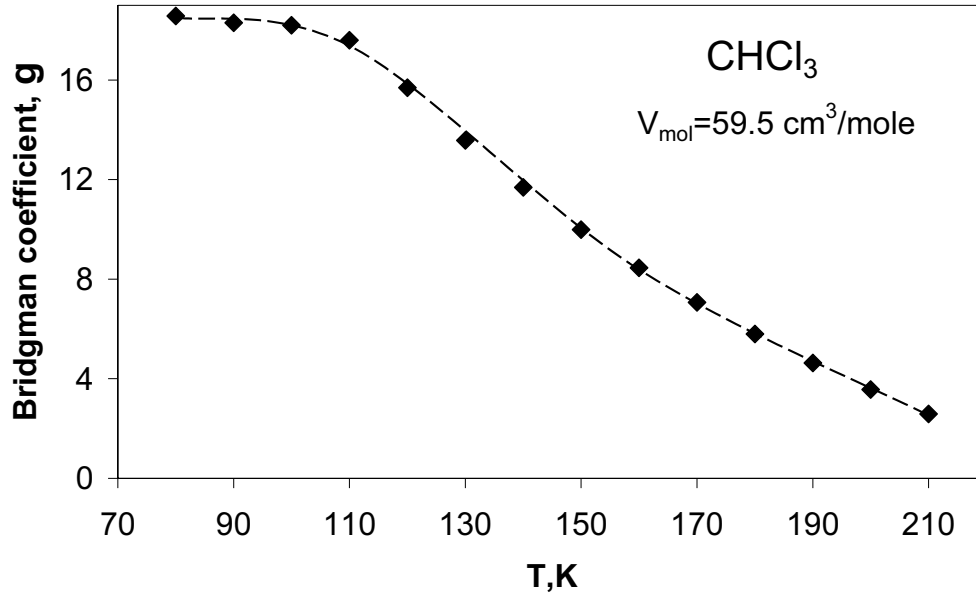


Fig.2. Calculated temperature dependence of the Bridgman coefficient.

The calculations were done using the values $\gamma=3.1$ [7] and $q=1$ (at $T \geq \Theta_D$, it is usually admitted that the second Grüneisen coefficient $q \approx 1$ [10,11]). Equation (13) describes the general tendency of the Bridgman coefficient to decrease as more of heat is being transported by “diffusive” modes.

5. Conclusion

It is shown that the temperature and volume dependences of the isochoric thermal conductivity of CHCl_3 can be explained 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 phonon mobility edge ω_0 is determined from the condition, that the phonon mean free path restricted by the Umklapp processes cannot become smaller than half the phonon wavelength. The Bridgman coefficient is estimated average over these modes, their volume dependences being strongly different. On the basis of these studies, it seems justified to deduce that the main reason for the essential deviations of the isochoric thermal conductivity of CHCl_3 from the dependence $1/T$ is the additional heat transfer by “diffusive” modes. The latter results from the thermal conductivity approaching its lower limit.

Acknowledgements

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