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Temperature and volume dependence of the thermal conductivity of solid $CHCl_3$

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Abstract. The temperature and volume dependences of the thermal conductivity of solid $CHCl_3$ are analyzed within the Debye model, under supposition that the phonon mean free path is approximately equal to one half of the wavelength. A quantitative description is given under assumption that 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.

PACS. 66.70.+f Nonelectronic thermal conduction and heat-pulse propagation in solids – 63.20.Ls Phonon interactions with other quasiparticles

1 Introduction

Heat transfer in dielectric crystals is realized through the transfer of phonons, quanta of energy associated with lattice vibrations. At temperatures of the order or higher than the Debye temperature (Θ_D), heat transport in simple atomic crystals is adequately described by a number of the classical theoretical models [1]. As compared to atomic solids the heat transfer in molecular crystals has a number of special features. One of these features that can affect the temperature dependence of the thermal conductivity is translation-rotation coupling.

The theory of three-phonon scattering [1] predicts that the lattice thermal conductivity should be inversely proportional to temperature ($\Lambda \propto 1/T$) at $T \geq \Theta_{\rm D}$, whereas the experimental thermal conductivity of molecular crystals shows considerable deviations from the above dependence [2]. The main reason for the observed deviations is an approach of thermal conductivity to its lower limit at premelting temperatures. The lower limit of thermal conductivity $\Lambda_{\rm min}$ is reached, when the heat is transferred through a random walk of the thermal energy between the weakly localized quantum mechanical oscillators, the lifetime of each is assumed to be half the period of vibration.

The purpose of this paper was to study basic features of heat transfer in the orientationally ordered phases 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. In this study we analyzed the temperature and volume dependences of isochoric thermal conductivity of $CHCl_3$ using the model, which assumed that the heat is transferred by low-frequency phonons and high-frequency "diffusive" modes.

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2 The object

Solid chloroform ($CHCl_3$) has only one crystallographic modification under the pressure of its own saturated vapor: 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 $\rm cm^{-1}$ (86 K) and partially overlap the librational modes in the 60–100 $\rm cm^{-1}$ band (86–144 K). The dipole moment of the $CHCl_3$ molecules is 1.01 D. Nuclear quadrupole resonance on the ^{35}Cl nuclei has been observed in $CHCl_3$ up to the melting temperature $T_m = 209.7$ K [5]. These data indicate that there are no molecular reorientations at frequencies above 10^4 $\rm s^{-1}$. The high entropy of melting, $\Delta S_f/R = 5.4$, also attests to a high degree of ordering in $CHCl_3$ [6]. At present, the thermal conductivity of solid $CHCl_3$ had been measured at constant pressure in the temperature range from 80 K to the melting temperature [2] and on several isochores above 175 K [7].

3 The model

To account for temperature dependence of the isochoric thermal conductivity in solid $CHCl_3$ we use the Debye

model of thermal conductivity [1] and took into consideration the assumption [8] that the lower limit for the phonon mean free path is of the order one half of the phonon wavelength:

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

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

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

and

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

where the Grüneisen parameter $\gamma = -(\partial \ln \Theta_D / \partial \ln V)_T$, m is the average atomic or molecular weight. When the temperature rises, the phonon mean free path decreases and can become comparable with the phonon wavelength. According to the model proposed in reference [8], the mean free path of phonons which frequencies are lager then ω_0 becomes constant and comparable with an interatomic distance, whereas the mean free path of low-frequency phonons is determined by equation (2) as before. Expression (2) is not applicable if $l(\omega)$ becomes of order or smaller than half of the phonon wavelength $\lambda/2 = \pi\upsilon/\omega$:

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

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

$$\frac{\upsilon}{AT\omega_0^2} = \frac{\alpha\pi\upsilon}{\omega_0}, \tag{5}$$

it is equal to

$$\omega_0 = 1/\alpha\pi AT. \tag{6}$$

The condition (5) 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 at al. [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

$$\Lambda = \Lambda_{\rm ph} + \Lambda_{\rm dif}. \tag{7}$$

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

$$\Lambda_{\rm ph} = \frac{k_B \omega_0}{2\pi^2 \upsilon A T}, \tag{8}$$

$$\Lambda_{\rm dif} = \frac{\alpha k_B}{4\pi\upsilon}\left(\omega_D^2 - \omega_0^2\right), \tag{9}$$

4 Results and discussion

As mentioned above, at temperature close to or above the Debye temperature the thermal conductivity of perfect dielectric crystals is determined solely by phonon-phonon scattering and it is expected to follow the law $\Lambda \propto 1/T$ [1]. 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]. It was found that the isochoric thermal conductivity of a number of molecular crystals changes slowly than suggested by the $1/T$ law [2,12–15]. This is connected with the fact that the mean free path of phonons becomes comparable to the intermolecular distance at premelting temperatures and the thermal conductivity reaches its lower value $\Lambda_{\rm min}$. The absolute value of $\Lambda_{\rm min}$ can be calculated in the framework of the Einstein model of diffusive heat transfer directly from site to site [9]

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

where $\Theta_D = \upsilon\left(\hbar/k_B\right)\left(6\pi^2 n\right)^{1/3}$, and n is the number of atoms (molecules) per unit volume. The calculated values of $\Lambda_{\rm min}$ were as a rule appreciably smaller than experimental ones [2,12,13]. The most obvious reason for such difference is that the site to site transfer of the rotational energy was not taken into account. In molecular crystals, heat is transferred by mixed translation-rotation modes, whose heat capacity is saturated in proportion to the total molecular degrees of freedom. Taking into account this feature, lower limit of the thermal conductivity can be expressed as [12]

$$\Lambda^*_{\rm min} = \frac{1}{2}\left(\frac{\pi}{6}\right)^{1/3}\left(1 + \frac{z}{3}\right) k_B n^{2/3}\left(\upsilon_\ell + 2\upsilon_t\right), \tag{11}$$

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

Thermal conductivity data of solid $CHCl_3$ [2] are presented in Figure 1 (squares). The values of isochoric thermal conductivity $\Lambda_{\rm v}$ correspond to a volume $V_{mol} = 59.5$ cm^3/mole [2]. As the temperature increases, the isochoric thermal conductivity of solid CHCl3 decreases according to the dependence $\Lambda \propto T^{-0.8}$.

In Figure 1, the data are also compared to the minimum thermal conductivity calculated according to equations (10, 11). In the Debye model $\Lambda_{\rm min}$ is determined only

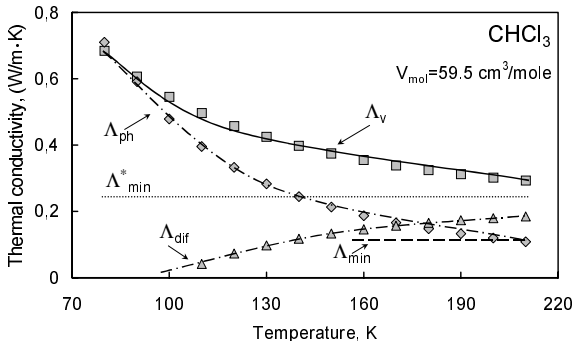

Fig. 1. Isochoric thermal conductivity $\Lambda_{\rm v}$ of solid $CHCl_3$ (squares) [2]. The solid line is the fitting curve for isochoric thermal conductivity. $\Lambda_{\rm ph}$ and $\Lambda_{\rm dif}$ are contributions of phonons and "diffusive" modes to heat transfer, respectively. The lower limits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

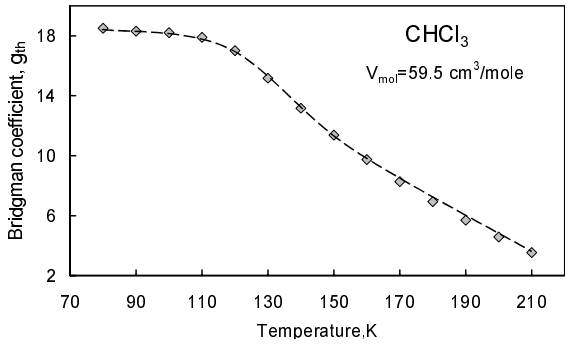

Fig. 2. Calculated temperature dependence of the Bridgman coefficient g.

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_{mol}, cm^3/mole	a, 10^{-10}m	υ, m/s	α	A, 10^{-16} s/K	$g_{\rm exp}$	$g_{\rm th}$
59.5	4.72	1310	2.45	1.20	3.9	3.54

by the sound velocities and density. The above model successfully describes the thermal conductivity of amorphous solids and strongly disordered crystals at $T \geq \Theta_{\rm D}$ [9]. Hence we emphasize that the calculated $\Lambda_{\rm min}$ is not the rigorous minimum but the rather an estimate of the lowest possible thermal conductivity for the materials. To our knowledge, no information is available on the sound velocity in solid $CHCl_3$. In this respect, the sound velocity (Tab. 1) was calculated by the method described in reference [16]. The necessary initial data were taken from [3–6]. The Debye temperature (86 K) was estimated from the boundary frequency of translational modes [4].

The discussion about the lower limit of thermal conductivity in molecular crystals brings up the inevitable question: whether the site-to-site transport of the rotational energy should be taken into account? The dotted line in Figure 1 shows the lower limit of thermal conductivity $\Lambda^*_{\rm min}$ (11) calculated taking into account the possibility of site to site rotational energy transfer. The minimal values of thermal conductivity $\Lambda_{\rm v}$ (Fig. 1) are 1.3 times higher than $\Lambda^*_{\rm min}$ calculated by equation (11), and 2.7 times higher than $\Lambda_{\rm min}$ calculated by equation (10).

To fit experimental data obtained in reference [2] for a solid $CHCl_3$, we use equations (7–9) with ω_0 given by equation (6). The fitting was performed by the computer simulation varying the coefficient A and α. The parameters of the Debye model for thermal conductivity used in the fitting (a, υ), and the fitted values A and α are listed in Table 1 along with the Bridgman coefficients obtained in the experiment (g_{exp}) [7] and calculated (g_{th}) within this model.

The fitting results for isochoric thermal conductivity are shown in Figure 1 (solid line). The same figure shows the contributions (dot-and-dash lines) to the heat transfer from the low-frequency phonons $\Lambda_{\rm ph}$ and the high-frequency "diffusive" modes $\Lambda_{\rm dif}$ (calculated by Eqs. (8, 9)). It is seen (Fig. 1) that the "diffusive" behavior of the oscillatory modes appears above 100 K. As temperature rises, the amount of heat transferred by the "diffusive" modes increases.

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

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

Using equations (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:

$$g_{\rm th} = \frac{\Lambda_{\rm ph}}{\Lambda} g_{\rm ph} + \frac{\Lambda_{\rm dif}}{\Lambda} g_{\rm dif}, \tag{13}$$

where

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

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

$$\gamma_0 = 3\gamma + 2q - 1/3. \tag{16}$$

As seen in Table 1, the experimental [7] and calculated (13) Bridgman coefficients are in quite good agreement. The temperature dependence of the Bridgman coefficient of solid $CHCl_3$ is shown in Figure 2. The calculation was 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

In summary, we can argue that the present analysis gives satisfactorily account for the observed temperature and volume behavior of the thermal conductivity. The noteworthy findings include: in the high-temperature region the temperature and volume dependence of $\Lambda_{\rm v}$ can be explained within a model in which the heat is transferred by phonons and above the phonon mobility edge ω_0 by "diffusive" modes migrating randomly from site to site. Or, in other words, the high-temperature behavior of $\Lambda_{\rm v}$ is determined by the balance between phonons and "diffusive" modes contributions to the total heat transfer. It is stressed that the heat transfer by high-frequency "diffusive" modes dominates in $CHCl_3$ at premelting temperatures, and their contributions to thermal conductivity is significant. The Bridgman coefficient is weighted average over these modes whose volume dependences are strongly different.

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