THERMAL CONDUCTIVITY OF SOLID CH$_2$Cl$_2$

O. I. Pursky
Technological State University of Cherkasy,
460 Shevchenko Blvd., Cherkasy, UA-18006, Ukraine
(Received November 15, 2005; received in final form February 16, 2006)

The isobaric thermal conductivity of solid CH$_2$Cl$_2$ was investigated by the linear-flow method under saturated vapor pressures in the temperature range from 80 K to the corresponding melting temperature and then recalculated for a constant density of the samples. The temperature dependence of the isobaric thermal conductivity of solid CH$_2$Cl$_2$ is 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 pressure dependence of the thermal conductivity of solid CH$_2$Cl$_2$ has been obtained.

Key words: heat transfer, thermal pressure, phonons, "diffusive" modes.

PACS number(s): 66.70.+f; 63.20.Ls

I. INTRODUCTION

The results of the research of the high-temperature (at the temperatures close to or above the Debye temperature $T \geq \Theta_D$) thermal conductivity of molecular crystals [1–3] point to some features which go beyond the framework of traditional ideas about heat transfer processes in dielectric crystals. According to the theoretical predictions [4–6], at $T \geq \Theta_D$ the lattice thermal conductivity should be inversely proportional to the temperature $\Lambda \propto 1/T$. It is usually admitted that in dielectric crystals the heat is transferred by phonons, which are quanta of energy of every vibrational mode. In the quantum picture, such transferring processes could be described through the destruction of some quanta of elastic energy, and the creation of new ones. The most likely processes is three-quantum scattering in which two quanta are destroyed and one created or vice versa.

To obey the $1/T$ law, the volume of crystals should remain invariable, because the modes would otherwise change and so would the temperature dependence of the thermal conductivity. However, the experimental results for isobaric thermal conductivity $\Lambda_v$ of molecular crystals show considerable deviations from the $1/T$ dependence [1–3,7,8]. 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 of molecular crystals were not taken into account in them. One of these features that can affect the temperature dependence of the thermal conductivity is the translation-rotation coupling. 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 thermal conductivity to approach its lower limit. As temperature increases, the phonon–phonon scattering processes enhance and the phonon mean-free path decreases, but it cannot become smaller than half the phonon wavelength $\lambda/2$ [9]. If all vibrational modes scatter for a distance of $\lambda/2$, the thermal conductivity reaches its lower limit $\Lambda_{\text{min}}$:

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

The summation is over three (one longitudinal and two transverse) sound modes with the sound velocities $v_1$, $\Theta_i$ is the Debye cut-off frequency for each polarization in Kelvins: ($\Theta_i = v_i (\hbar / k_B) (6\pi^2 n)^{1/3}$), $n = 1/a^3$ is the number of atoms per unit volume, $a$ is the lattice parameter. The calculated values of $\Lambda_{\text{min}}$ (1) were as a rule considerably smaller than experimental ones [2,8,10,11]. The most obvious reason for this difference is that the site to site transfer of the rotational energy was not taken into account. In molecular crystals the heat is transferred by mixed translation-rotation modes, whose heat capacity is saturated in proportion to the total molecular degrees of freedom [12]. Taking into account this feature of molecular crystals, lower limit of the thermal conductivity can be represented as [10]

$$\Lambda_{\text{min}}^* = \frac{1}{2} \left(\frac{\pi}{3}\right)^{1/3} \left(1 + \frac{z}{3}\right) k_B n^{2/3} (v_L + 2v_T)$$  \hspace{1cm} (2)

where $v_L$ and $v_T$ are the longitudinal and transversal sound velocities, respectively, $z$ is the number of rotational degrees of freedom.

The purpose of this paper was to study basic features of high-temperature heat transfer in solid CH$_2$Cl$_2$.

II. THE OBJECT

The solid CH$_2$Cl$_2$ under the pressure of its own saturated vapor has only one crystallographic modification. It has orthorhombic spatial symmetry $P_{bcn}$ with four molecules per unit cell [13–15]. It is known from the Raman spectrums and IR absorption (20 K and 77 K)
data [16,17] that the translational modes take the frequency band up to 80 cm\(^{-1}\) and partially overlap the librational modes in the 70-150 cm\(^{-1}\) (100-210K). The dipole moment of the CH\(_2\)Cl\(_2\) molecule is 1.6\(D\). The lower intramolecular mode corresponds to the frequency of 285 cm\(^{-1}\) (410 K). Nuclear quadrupole resonance (NQR) on the \(^{35}\)Cl nuclei has been observed in CH\(_2\)Cl\(_2\) up to melting temperature \(T_m = 176.3\) K [18]. These data also indicate that there are no molecular reorientations at frequencies above 10\(^4\) sec\(^{-1}\).

To date, the thermal conductivity of solid CH\(_2\)Cl\(_2\) has been measured at premelting temperatures on several isochores [19].

III. ISOBARIC THERMAL CONDUCTIVITY AND EXPERIMENTAL TECHNIQUE

The isobaric thermal conductivity \(\Lambda_p\) of solid CH\(_2\)Cl\(_2\) was investigated by the linear-flow method [8] under saturated vapor pressure in the temperature range from 80 K to the corresponding melting temperature. The measurement ampoule, in which the sample was grown, was a tube of Kh18N9T stainless steel with the length of 70 mm and an inner diameter of 7.2 mm. The temperature sensors were germanium resistance thermometers and a Copper–Constantan thermocouple, which were mounted on copper rings attached to the cell. The measurements were made by a modified heat potentiometer [20], which made it possible to minimize the error in determination of the thermal conductivity. Uncontrolled heat fluxes due to thermal radiation were reduced considerably with a radiation shield, on which a system of thermocouples and a precision heat controller reproduced the temperature field of the measuring cell. The polycrystalline samples were grown from the gas phase at the temperature field of the measuring cell. The samples had a granular structure. Most of the grains were of 1.5 to 3 mm in the linear size. The measurements were conducted on two samples of 99.8% purity. The accuracy of the thermal conductivity measurement is 5%.

The results of the measurements are presented in Fig. 1. The different symbols correspond to the two different samples. The solid line shows smoothed values for isobaric thermal conductivity. The dashed line in the lower part of Fig. 1 is the lower limit of the thermal conductivity \(\Lambda_{\text{min}} (1)\) calculated for the isobaric case according to Cahill and Pohl, in the framework of the Einstein model of diffusional heat transfer directly from atom to atom [9]. From Fig. 1 it can also be noted that at premelting temperatures the experimental thermal conductivity approaches its lower limit, being no more than twice that values \(\Lambda_{\text{min}} (1)\). The isobaric thermal conductivity of solid CH\(_2\)Cl\(_2\) decreases with an increase in the temperature as \(\Lambda_p \propto T^{-1.21}\). Such a dependence of isobaric thermal conductivity is typical for simple molecular crystals [1,8]. It can be related to two major reasons. Firstly, the isobaric thermal conductivity also depends upon a thermal expansion of samples [12]. The second reason related to nearing thermal conductivity to its lower limit. The temperature dependence of isobaric thermal conductivity can be described in the framework of Leibfried & Schlümann formula [4] taking into account thermal expansion of samples.

![Fig. 1. Isobaric thermal conductivity \(\Lambda_p\) of solid CH\(_2\)Cl\(_2\). The solid lines are the fitting curves for isobaric thermal conductivity. The lower limit of thermal conductivity \(\Lambda_{\text{min}} (1)\) is calculated for the isobaric case, in the framework of the Einstein model of diffusional heat transfer directly from atom to atom [9].](image)

IV. ISOCHORIC THERMAL CONDUCTIVITY

To compare correctly experimental results of thermal conductivity with theory it is necessary to use data at constant density to exclude the effect of thermal expansion. In accordance with this assertion, the experimental results were recalculated to a constant volume of samples \(V_\text{mol} = 47.1\) cm\(^3\)/mole [19], which are occupied by the samples at the growth temperature (80 K). The calculations were performed according to the formula [12]:

\[
\Lambda_v = \Lambda_p \left( \frac{V(T)}{V_0} \right)^g,
\]

where \(\Lambda_v\) is the isochoric thermal conductivity, \(V(T)\) is the current molar volume of the free sample [21], \(V_0\) is the molar volume for which the recalculation is carried out, and \(g = - (\partial \ln \Lambda / \partial \ln V)_{P} \) is the Bridgman coefficient (Tab. 1) [21]. Figure 2 shows the isochoric thermal conductivity recalculated to the corresponding molar volume (black squares). Recalculation results are in good agreement with isochoric data cited in [19] for the same conditions \((P,T,V)\). The isochoric thermal conductivity of solid CH\(_2\)Cl\(_2\) decreases with increasing temperature slower than suggested by the \(\Lambda \propto 1/T\) (\(\Lambda_{\text{CH}_2\text{Cl}_2} \propto T^{-0.88}\)). The last one, qualitatively conforms
THERMAL CONDUCTIVITY OF SOLID CH$_2$Cl$_2$

to the case of strong phonon scattering, when mean free path of vibrational modes are substantially limited and approaches to phonon wavelength. In this respect, to elucidate the reasons for such deviations isochoric thermal conductivity from the dependence $1/T$, we used Debye model of the heat transfer [4] and assumption of Roufousse and Klemens [21] about lower limit of the phonon scattering length. According to the Debye formalism, the lattice thermal conductivity can be expressed as

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

where $\omega_D$ is the Debye frequency ($\omega_D = (6\pi^2)^{1/3}v/a$), $l(\omega)$ is the phonon mean free path, and $\omega$ 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

$$l_u(\omega) = \nu/AT\omega^2,$$

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

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

Expression (6) is not applicable if $l(\omega)$ becomes of the 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 [21]. Let us assume that in the general case

$$l(\omega) = \begin{cases} \frac{\nu}{AT\omega^2} , & 0 \leq \omega \leq \omega_0, \\ \frac{\alpha \pi v}{\omega} , & \omega_0 < \omega \leq \omega_D, \end{cases}$$

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

$$\frac{\nu}{AT\omega_0^2} = \frac{\alpha \pi v}{\omega_0},$$

It equals

$$\omega_0 = 1/\alpha \pi AT,$$

Condition (8) is a 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 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. Substituting (5) in (4) we have the known $1/T$ law:

$$\Lambda_{ph} = \frac{k_B \omega_D}{2\pi^2 v AT},$$

At $\omega_0 \leq \omega_D$ the integral of thermal conductivity (4) is subdivided into two parts describing the contributions to the heat transfer from the low-frequency phonons and high-frequency “diffusive” modes:

$$\Lambda = \Lambda_{ph} + \Lambda_{dif},$$

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

$$\Lambda_{ph} = \frac{k_B \omega_0}{2\pi^2 v AT},$$

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

Fig. 2. Isochoric thermal conductivity $\Lambda_\nu$ of solid CH$_2$Cl$_2$ (squares). The solid line is the fitting curve for isochoric thermal conductivity. $\Lambda_{ph}$ and $\Lambda_{dif}$ are relative contributions of phonons and “diffusive” modes, calculated according to Eqs. (12), (13). The lower limit of thermal conductivity $\Lambda_{\nu \min}$ (2) is calculated taking into account the possibility of the site to site rotational energy transfer.

<table>
<thead>
<tr>
<th>$a$, $10^{-10}$ m</th>
<th>$c$, m/s</th>
<th>$\gamma$</th>
<th>$\alpha$</th>
<th>$A$, $10^{-16}$ s/K</th>
<th>$g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>1770</td>
<td>2.9</td>
<td>1.7</td>
<td>1.33</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table 1. Debye model parameters of thermal conductivity used in fitting and other quantities which were used for the calculation.
To our knowledge, no information at all is available on the velocity of sound in solid CH₂Cl₂. In this respect, the phonon velocity (Table 1) was calculated by the method described in [22,23]. The Debye temperature was determined by using the boundary frequency of translational modes from the Raman and IR absorption data at 20 K. The necessary initial data were taken from [16,17].

The computer fitting of the thermal conductivity using Eqs. (11–13) was performed by the least square method, varying the coefficients $A$ and $\alpha$. The parameters of the Debye model for thermal conductivity used in the fitting $(\alpha, \nu)$, and the fitted values $A$ and $\alpha$ are listed in Table 1 along with the Bridgman coefficient obtained in the experiment [19].

The fitting results for isochoric thermal conductivity are shown in Fig. 2 (solid line). 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 Eqs. (12), (13)). The dotted line shows the lower limit of thermal conductivity $\Lambda_{\text{min}}$ (2) calculated of taking into account the possibility of site to site rotational energy transfer. It is seen (Fig. 2) that in solid CH₂Cl₂ the “diffusive” behavior of the oscillatory modes starts above 90 K. As temperature rises the amount of heat transferred by the “diffusive” modes increases. Above 150 K most of the heat is transported by “diffusive” modes. It can be seen from Fig. 2 that the results obtained by using the above model fit the experimental results well and maximum differences do not exceed 5%. The minimal values of thermal conductivity $\Lambda_V$ (Fig. 2) is 1.04 times higher than $\Lambda_{\text{min}}$ calculated by Eq. (2), and 1.5 times higher than $\Lambda_{\text{min}}$ calculated by Eq. (1). 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 $\Lambda_{\text{min}}$ and $\Lambda_{\text{min}}$ suggests the positive answer.

\begin{equation}
\left(\frac{\partial P}{\partial T}\right)_V = \gamma C_V V_{\text{mol}}, \tag{14}
\end{equation}

The necessary initial data were taken from [19]. As is seen from Fig. 3, the thermal pressure in the isochoric sample $(V_{\text{mol}}=47.1 \ \text{cm}^3/\text{mole})$ changes by more than two orders of magnitude in the temperature range under investigation. The molar volume of the samples depend on their growth temperature. The results of calculations are in good agreement with the data obtained from direct measurement of the thermal pressure in solid CH₂Cl₂ [19] at premelting temperatures.

![Fig. 3. Temperature dependence of thermal pressure for samples of solid CH₂Cl₂ with various molar volumes. Line 1 corresponds to experimental data [21].](image)

![Fig. 4. Temperature dependence of isochoric thermal conductivity of solid CH₂Cl₂ with various molar volumes. Line 1 corresponds to the data of direct measurements of the isochoric thermal conductivity [21] at premelting temperatures.](image)

The temperature dependences of the isochoric thermal conductivity $\Lambda_V$ (Fig. 4) for the samples of solid CH₂Cl₂ with various molar volumes (these dependences are needed afterwards to obtain the pressure dependence of thermal conductivity $\Lambda_T(P)$) were calculated according to formula (3). Using the temperature dependences of the thermal pressure $P(T)$ (Fig. 3) and the isochoric ther-
The thermal conductivity (Fig. 4), were constructed the dependences $A_T(P)$ of the thermal conductivity on the pressure that arises in the studied samples as their volume changes. The results are displayed in Fig. 5. Using the methods of computer simulation, the thermal conductivity of CH$_2$Cl$_2$ was revealed to vary, as the pressure grows, according to the dependence

$$ A_T = B(T) + C(T)P + D(T)P^2, \quad (15) $$

where $B$, $C$, and $D$ are numerical coefficients, the values of which are listed in Table 2. With the increase in pressure at constant temperature, the thermal conductivity also increases (Fig. 5). The coefficient $B$ is nothing else but the value of isobaric thermal conductivity. In equation (15) the coefficients $C$ and $D$ determine the influence of pressure on the thermal conductivity. By matching the units of the $C$ and $D$ coefficients with those of thermal conductivity it is not difficult to notice that the coefficients $C$ and $D$ can be determined as partial derivatives $(\partial A/\partial P)_T$ and $(\partial^2 A/\partial P^2)_T$, respectively. Then dependence (15) can be written as

$$ A_T = A_P + \left( \frac{\partial A}{\partial P} \right)_T P + \left( \frac{\partial^2 A}{\partial P^2} \right)_T P^2 \quad (16) $$

![Fig. 5. Pressure dependence of thermal conductivity of solid CH$_2$Cl$_2$. $P_0$ corresponds to the values of thermal conductivity under saturated vapor pressure.](image)

The verification of this dependence, on the example of the C$_6$H$_4$ and CCl$_4$ solids, gives good accordance with the direct research results of the pressure dependences of thermal conductivity [24,25] (in the pressure range from 0.1 GPa to 1.8 the GPa distinctions between calculation (16) and experimental values do not exceed 7%).

<table>
<thead>
<tr>
<th>$T$, K</th>
<th>$B$, W/(m·K)</th>
<th>$C$, W/(m·K·Pa)</th>
<th>$D$, W/(m·K·Pa$^2$)</th>
<th>$P$, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>0.443</td>
<td>0.0006</td>
<td>$-3 \times 10^{-7}$</td>
<td>0.0 ± 92.1</td>
</tr>
<tr>
<td>130</td>
<td>0.363</td>
<td>0.0004</td>
<td>$-3 \times 10^{-7}$</td>
<td>0.0 ± 153.5</td>
</tr>
<tr>
<td>150</td>
<td>0.306</td>
<td>0.0003</td>
<td>$1 \times 10^{-8}$</td>
<td>0.0 ± 214.9</td>
</tr>
<tr>
<td>170</td>
<td>0.263</td>
<td>0.0003</td>
<td>$3 \times 10^{-8}$</td>
<td>0.0 ± 276.3</td>
</tr>
</tbody>
</table>

Table 2. Isothermal pressure dependence of thermal conductivity of CH$_2$Cl$_2$ fitted to equations of the form of $A_T = B(T) + C(T)P + D(T)P^2$.

VI. CONCLUSIONS

The current study presents some results of the investigation of high-temperature thermal conductivity in the orientationally ordered phases of molecular crystals, with solid CH$_2$Cl$_2$ as an example. The isobaric thermal conductivity of solid CH$_2$Cl$_2$ has been investigated in the temperature interval from 80 K to the melting temperature and then recalculated for a constant density of samples. The obtained experimental data was used in the calculation mechanism, which was suggested to determine the pressure dependence of thermal conductivity.

It is shown that the temperature dependence of the isochoric thermal conductivity of CH$_2$Cl$_2$ can be described within a model in which the heat is transferred by phonons and above the phonon mobility edge by “difusive” modes migrating randomly from site to site. The phonon mobility edge $\omega_o$ is determined from the condition that the phonon mean free path restricted by the Umklapp processes cannot become smaller than half the phonon wavelength. It should be noted that the present model can be applied to the simulation of the isochoric thermal conductivity only in the orientationally ordered phases of molecular crystals, since thermal conductivity in the orientationally disordered phases of molecular crystals depends essentially on the character of the orientational molecular motion as well.


ТЕПЛПРОВІДНІСТЬ ТВЕРДОГО CH2Cl2

О. І. Пурскій
Черкаський державний технологічний університет,
вул. Шевченка, 460, Черкаси, 18006, Україна

Ізобарну теплопровідність твердого CH2Cl2 досліджено шляхом стаціонарним методом під тиском власних насичених парів у діапазоні температур від 80 К до температури плавлення. Результати експерименту перераховано до постійної густини зразків. Температурну залежність ізохорної теплопровідності твердого CH2Cl2 пояснено в моделях, у якій тепло переноситься фононами, але від ніших рухливості фононів — “дифузійними” модами, що мігрують випадково з вузла на вузол. Отримано залежність теплопровідності твердого CH2Cl2 від тиску.

342