Heat transfer in solid halogenated methanes: trifluoromethane

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The isochoric thermal conductivity of solid trifluoromethane was investigated for three samples of different densities in the interval from 75 K to the onset of melting. The isochoric thermal conductivity first decreases with increasing temperature, passes through a minimum at $T \sim 100$ K, and then starts to increase slowly. The results obtained are compared with the thermal conductivities of other freons of methane series. The correlation between the temperature dependence of isochoric thermal conductivity and the character of the rotational molecular motion is discussed.

PACS: 66.70.–f Nonelectronic thermal conduction and heat-pulse propagation in solids; thermal waves; 63.20.Kk Phonon interactions with other quasiparticles.

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Introduction

The solid freons of the methane series consisting of tetrahedral molecules are convenient objects to investigate the correlation between the rotational motion of molecules and the behavior of thermal conductivity. Methane (CH$_4$) and carbon tetrahalogenides (CF$_4$, CCl$_4$, CBr$_4$, C$I$$_4$) form high-temperature «plastic» or orientationally-disordered phases in which the rotational motion of molecules is similar to their motion in the liquid state [1,2]. In crystals consisting of lower-symmetry molecules such as chloroform (CHCl$_3$), methylene chloride (CH$_2$Cl$_2$) or dichlorodifluoromethane (CCl$_2$F$_2$) the forces of the noncentral interaction of molecules are much stronger and the long-range order usually persists in them up to the melting temperature. The relative simplicity of the freon molecules allows adequate interpretation of experimental results.

The orientational motion in molecular crystals can be either vibrational or rotational depending on the temperature and the relationship between the noncentral forces and the kinetic energy of rotation. At low temperatures the motion of molecules in molecular crystals is, with rare exception (quantum crystals), of oscillatory character: at $T \to 0$ molecules perform zero orientational vibrations about the equilibrium directions. As the temperature rises, the r.m.s. amplitudes of librations increase and the molecules can hop over the accessible orientations. This disturbs the long-range order and can provoke a phase transition. The degree of orientational order can be varied by changing the temperature and selecting crystals with different parameters of the molecular interaction, which permits us to investigate the influence of the rotational motion of molecules upon the thermal properties of the crystal, including its thermal conductivity.

It is best to measure thermal conductivity at a fixed density, which excludes the effect of thermal expansion and ensures a more adequate comparison with theory. This is particularly important at high temperatures when the thermal expansion coefficients are large. Previously, we investigated the isochoric thermal conductivity of CH$_4$ [3], CCl$_4$ [4], CHCl$_3$ and CH$_2$Cl$_2$ [5], CF$_2$Cl$_2$ and CHF$_2$Cl [6]. The regularities of the heat transport in simple molecular crystals (including the methane-series freons) depending on the rotational degrees of freedom of molecules at the Debye and higher temperatures ($T \approx Q_D$) can be generalized as follows. Because of the strong translational-orientational (TO) coupling in the orientationally-ordered phases [7], molecular librations contribute considerably to the thermal resistance $W = 1/\Lambda$ of the crystal. As a result, the isochoric thermal conductivity approaches its lower limit and deviates significantly from the dependence $\Lambda \propto 1/T$ (CHCl$_3$, CH$_2$Cl$_2$, and CF$_2$Cl$_2$).

The concept of the lower limit of thermal conductivity...
imply that $\lambda_{\text{min}}$ can be achieved if the heat transport is realized through thermal energy diffusion between the neighboring quantum-mechanical oscillators whose lifetime is about half the oscillation period [8]. On a weakly-retarded rotation, the translational-orientational component of the total thermal resistance decreases owing to weakening of TO coupling and the isochoric thermal conductivity can grow with temperature. We observed this effect in methane and carbon tetrachloride [3,4]. A weak growth of thermal conductivity was also found in the high-temperature phase of solid chlorodifluoromethane (CHF$_2$Cl) [6]. This behavior is not entirely clear for the lack of full information about the character of the rotational motion of the molecules in solid CHF$_2$Cl. According to calorimetric data [9], solid CHF$_2$Cl experiences a $\lambda$-type phase transition at 59 K and melts at 115.7 K with an entropy jump $\Delta S/R = 4.25$ ($R$ is gas constant).

Note that a crystal is defined as plastic if it obeys the Timmerman criterion: the melting entropy of phase I must be below $2.5R$. Calculation of the Debye temperature of CHF$_2$Cl from calorimetric data gives $(70 \pm 5)$ K. The crystal structure of CHF$_2$Cl was investigated at 10 and 70 K by the neutron scattering method [10]. The low-temperature phase is monoclinic; it has the spatial symmetry $P112/n$ ($C_{2h}^4$) and eight molecules in the cell. The high-temperature phase is tetragonal with the spatial symmetry $P4_2/n$ ($C_{3h}^4$) and it also has eight molecules in the cell. A shifting-type phase transition occurs at 59 K and has little effect on the position and orientation of the molecules. The object of this study was trifluoromethane (CHF$_3$). The molecule rotation at the lattice sites of CHF$_3$ was investigated previously by the NMR technique [11,12].

### Results and discussion

The isochoric thermal conductivity of solid trifluoromethane was investigated on three samples of different densities in the interval from 75 K to the onset of melting. The experimental results are shown in Fig. 1 (solid lines are smoothed thermal conductivity values; the dashed line shows the thermal conductivity measured under saturated vapor pressure). The molar volumes $V_m$, temperatures $T_0$ (onset of $V = \text{const}$ condition) and $T_m$ (onset of sample melting) are shown in Table 1. The Bridgman coefficients $g = -(\partial \ln \Lambda / \partial \ln V)_T$ calculated from the experimental results are $4.8 \pm 0.8$ at $T = 115$ K. Isochoric thermal conductivity of a free sample. Arrows mark the onset of the experimental condition $V = \text{const}$ and the onset of the sample melting.

![Fig. 1. The isochoric thermal conductivity of three solid CHF$_3$ samples of different densities: Nos. 1 ($\Lambda$), 2 (O), 3 (C) (see also Table 1). Solid lines show smoothed values of isochoric thermal conductivity. Dashed line and rhombus are for the thermal conductivity of a free sample. Arrows mark the onset of the experimental condition $V = \text{const}$ and the onset of the sample melting.](image-url)
conductivity first decreases with increasing temperature, passes through a minimum at $T \approx 100$ K, and then starts to increase slowly up to the onset of melting.

Trifluoromethane CHF$_3$ melts at $T_m = 117.97$ K, the melting entropy being $\Delta S/R = 4.14$ [14]. According to heat capacity data [14], there are no phase transitions in the interval 15–117 K. We estimated the Debye temperature ($\Theta_D = 88 \pm 5$ K) from the low-temperature part of these data. The existence of only one crystalline modification in the region 20–106 K is also supported by Raman and IR spectral investigations [15]. This points to the absence of strong hydrogen bonds in CHF$_3$. Neutron scattering investigations of the crystallographic structure of CHF$_3$ at 4.2, 40 and 70 K [16] revealed only one crystalline phase of the spatial symmetry $P2_1/c$ with four differently oriented molecules in the monoclinic cell.

Absorption line shapes of the NMR signal and the spin-lattice relaxation times were investigated on the $^1$H and $^{19}$F nuclei of CHF$_3$ at $T = 7–116$ K [11] and 4.2–120 K [12], respectively. It is found that above $T = 80$ K the second NMR moment decreases sharply from 11.5 G$^2$ to 3.0 G$^2$ immediately prior to melting, which suggests enhancement of the molecule rotation about the three fold axis. The activation energy of rotation and the preexponential Arrhenius factors were calculated to be 17.0 kJ/mol and 1.0 $\cdot 10^{-16}$ s [11], and 18.0 kJ/mol and (4.9–8.9) $\cdot 10^{-17}$ s [12], respectively. In Fig. 2 these results are presented as a logarithmic function of frequency of reorientations about the three fold axis versus the inverse temperature. The upper frequency of the lattice modes which correspond to $\Theta_D = 88$ K is shown at the top of Fig. 2. The data of the two studies are in good agreement. At the melting temperature the reorientation frequency is three orders of magnitude lower than the Debye frequency, which is rather surprising. The growth of thermal conductivity with temperature was observed previously in orientationally-disordered phases of methane and carbon tetrahalogenides, in which the molecule rotation is weakly hindered or almost free [1,2].

Table 2 gives a general information about the methane-series freons: melting temperatures $T_m$, phase transition temperatures $T_{I-II}$, structure and the number of molecules in the unit cell $z$, melting entropy $\Delta S/R$, Debye temperatures $\Theta_D$, Bridgman coefficients $g = -(\partial \ln \Lambda / \partial \ln V)_T$, dipole moments of molecules $\mu$. Included are also the data for CBr$_4$ (its thermal conductivity was measured in Ref. 17).

The isochoric thermal conductivity of orientationally-disordered phases in the methane-series freons increases with temperature. (The exception is methane in where the

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T_m$, K</th>
<th>$T_{I-II}$, K</th>
<th>$z$</th>
<th>$\Delta S/R$, J/mol K</th>
<th>$\Theta_D$, K</th>
<th>$g$, m$^2$ K$^3$/mol</th>
<th>$\mu$, D</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>90.6</td>
<td>6</td>
<td>4</td>
<td>1.24</td>
<td>96 (90 K)</td>
<td>8.8</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(II)</td>
<td>20.5</td>
<td>32</td>
<td>1.21</td>
<td>141 (0 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>250.3</td>
<td>363</td>
<td>4</td>
<td>1.3</td>
<td>92 (0 K)</td>
<td>6.0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(II)</td>
<td>225.5</td>
<td>32</td>
<td>1.3</td>
<td>62 (300 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBr$_4$</td>
<td>363</td>
<td>320</td>
<td>2/c</td>
<td>1.3</td>
<td>3.4</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(II)</td>
<td>59</td>
<td>P112/n</td>
<td>8</td>
<td>4.25</td>
<td>70 (0 K)</td>
<td>1.41</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>210</td>
<td>176</td>
<td>Pnna</td>
<td>4</td>
<td>5.4</td>
<td>86*</td>
<td>3.9</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>117</td>
<td>176</td>
<td>Pbcn</td>
<td>4</td>
<td>3.13</td>
<td>115*</td>
<td>4.6</td>
</tr>
<tr>
<td>CF$_2$Cl$_2$</td>
<td>115</td>
<td>176</td>
<td>Fd$ar{d}$</td>
<td>8</td>
<td>4.2</td>
<td>80*</td>
<td>5.0</td>
</tr>
<tr>
<td>CHF$_3$</td>
<td>118</td>
<td>118</td>
<td>P21/c</td>
<td>4</td>
<td>4.14</td>
<td>88*</td>
<td>4.6</td>
</tr>
</tbody>
</table>

*Estimates obtained from IR and Raman spectra for the upper boundary of the lattice modes.
thermal conductivity has a maximum and then starts to decrease [3].) This is because the translational-orientational component of the total thermal resistance decreases sharply as the rotation of the molecules becomes weakly hindered. In some crystals with reorientation frequencies up to $10^4$ s$^{-1}$ (CHCl$_3$, CH$_2$Cl$_2$ and CF$_2$Cl$_2$) the isochoric thermal conductivity approaches its lower limit $\Lambda_{\text{min}}$ [5,6] and deviates significantly from the dependence $\Lambda \propto 1/T$.

Apart from CHF$_3$, a weak growth of isochoric thermal conductivity with temperature was also observed in CHF$_2$Cl (I) [6]. However, in the latter case only the Raman spectra were investigated at $T = 20–80$ K [18] and NMR data are unavailable. The lattice modes exhibit distinct peaks at $T = 20$ K and broad overlapping bands at $T = 80$ K, which are more common for orientationally-disordered crystals. At 20 K there were three split peaks in the interval 30–50 cm$^{-1}$ (43–72 K) and three split peaks in the region 55–80 cm$^{-1}$ (79–115 K). They were presumably assigned to the translational and librational modes, respectively. The upper boundary of the translational modes agrees well with the Debye frequency obtained from calorimetric data. However, the analysis of the spectra of the intramolecular modes at 80 K reveals no disordered structure. The observed picture might therefore be a result of broadening and re-overlapping of the corresponding components. We can expect intensive reorientational motion in solid CHF$_2$Cl at least about the C–Cl axis.

The weak growth of isochoric thermal conductivity with temperature in solid CHF$_3$ and CHF$_2$Cl suggests that the translational-orientational coupling becomes weaker in these crystals at premelting temperatures owing to the intensive molecular reorientations about the three fold axes. It is rather surprising that in CHF$_3$ the reorientation frequency is much lower than the boundary Debye one. This fact calls for further theoretical studies. At present there is no general theory that could relate the behavior of thermal conductivity to the character of the orientational motion of molecules in molecular crystals.

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