

Thermal conductivity of solid CF_2Cl_2

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The thermal conductivity of solid CF_2Cl_2 was measured by the linear-flow method in the temperature range 80–115 K under saturated vapor pressure. Special attention is given to the explanation of the heat transfer process under constant density. The temperature dependence of the isochoric thermal conductivity is analyzed within a model in which heat is transferred by phonons and, above the phonon mobility edge, by «diffusive» modes migrating randomly from site to site.

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

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1. Introduction

The solid freons of the methane series are convenient objects for analyzing the effect of rotational degrees of freedom of molecules and their symmetry on the behavior of the thermal conductivity of crystals [1]. Depending on the material and temperature, the form of orientational motion in these solids changes over a wide range, i.e., from librations at small angles to hindered or practically free rotation. The crystals consisting of high-symmetry molecules like CH_4 , CF_4 , CCl_4 , and CBr_4 form high-temperature «plastic» or orientationally disordered phases, in which the rotational motion of molecules resembles their motion in the liquid state. In crystals consisting of molecules of a lower symmetry the long-range orientational order persists, as a rule, up to the melting point. The relative simplicity of these materials enables an appropriate theoretical interpretation.

The present paper gives an account of studies of thermal conductivity in solid CF_2Cl_2 . Both isobaric and isochoric thermal conductivities [2] of solid CF_2Cl_2 differ essentially from the law $\Lambda \propto 1/T$, which is usually expected at $T \geq \Theta_D$ (Θ_D is the Debye temperature).

2. Results and discussion

The solid CF_2Cl_2 melts at 115.2 K. It has only one crystallographic modification: orthorhombic, space symmetry F_{dd2} with eight molecules per unit cell [3]. It is known from the Raman spectra and IR absorption [4] that

the translational modes extend up to 50 cm^{-1} (79 K) and partially overlap the librational modes located above. The dipole moment of the CF_2Cl_2 molecule is $0.51D$. Unfortunately, no experimental data are available on sound velocity, elastic constants, heat capacity, and thermal expansion of solid CF_2Cl_2 . According to the measurements cited in [1], the molar volume of solid CF_2Cl_2 at the triple point is $60.8 \text{ cm}^3/\text{mole}$. To date, the thermal conductivity of solid CF_2Cl_2 has been measured at premelting temperatures on several isochores [1], but no theoretical analysis was suggested.

The isobaric thermal conductivity Λ_p of solid CF_2Cl_2 was studied by the linear-flow method in the temperature range 80–115 K under saturated vapour pressure. The measurement ampoule was 70 mm long stainless steel a tube with an inner diameter of 7.2 mm. The temperature sensors were germanium resistance thermometers and a copper–constantan thermocouple mounted on copper rings attached to the cell. The measurements were carried out by a modified heat potentiometer [5], which made it possible to minimize the error in determination of the thermal conductivities. Uncontrolled heat fluxes due to thermal radiation were reduced considerably with a radiation shield, on which the 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 a pressure of around 1.6 bar, with the temperature

of the bottom of the measuring ampoule maintained close to the temperature of liquid nitrogen. The growth took around 6 hours. The measurements were carried out on two samples of 99.8% purity. The accuracy of thermal conductivity measurements is 5%.

The experimental results are shown in Fig. 1. The different symbols correspond to two different samples. The solid line shows smoothed values. Our data are in good agreement with earlier results for the same condition (P, T) [1]. The line in the lower part of Fig. 1 is the lower limit of thermal conductivity Λ_{\min} calculated for the isobaric case according to Cahill and Pohl, in the framework of the Einstein model of diffusive heat transfer [6]. The isobaric thermal conductivity of solid CF_2Cl_2 decreases with increasing temperature as $\Lambda_p \propto T^{-1.12}$. The major reason of this phenomenon is an influence of thermal expansion [7].

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. Previously, the isochoric thermal conductivity of solid CF_2Cl_2 was studied at different molar volumes in the temperature interval 96–128 K [1]. The corresponding experimental data for the sample with molar volume $59,9 \text{ cm}^3/\text{mole}$ are shown in the Fig. 2 (black squares). The isochoric thermal conductivity of solid CF_2Cl_2 decreases with increasing temperature approximately as $\Lambda_V \propto T^{-0.2}$. The latter qualitatively conforms to the case of strong phonon scattering, when the mean-free path of vibrational modes is strongly limited and approaches the phonon wavelength. To provide an explanation for such temperature dependence of the isochoric thermal conductivity we used the model that described in [8]. The thermal conductivity can be represented as [2]

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

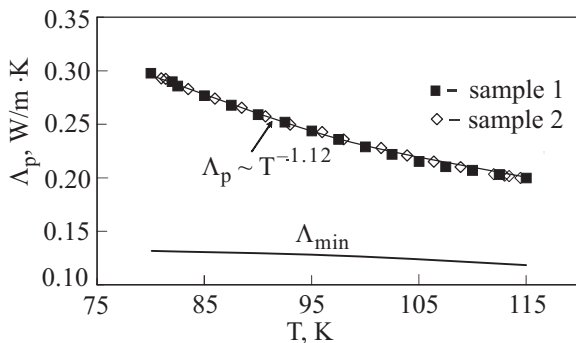


Fig. 1. Isobaric thermal conductivity Λ_p of solid CF_2Cl_2 . The solid line shows smoothed values of the isobaric thermal conductivity. The lower limit of thermal conductivity Λ_{\min} is calculated in the framework of the Einstein model of diffusive heat transfer according to Eq. (7).

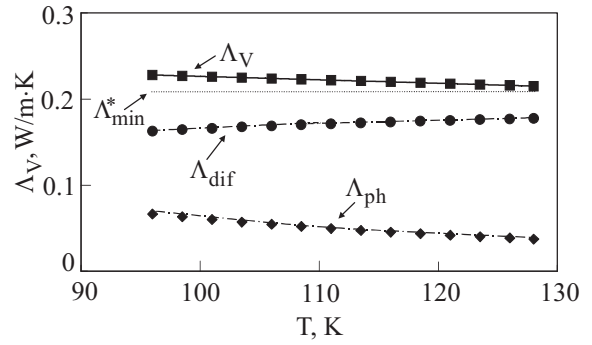


Fig. 2. Isochoric thermal conductivity Λ_V of solid CF_2Cl_2 for the sample with molar volume $59,9 \text{ cm}^3/\text{mole}$ (squares) [1]. The solid line is the fitting curve for isochoric thermal conductivity. Λ_{ph} and Λ_{dif} are relative contributions of phonon and «diffusive» modes, calculated according to Eqs. (5),(6). The lower limit of thermal conductivity Λ_{\min}^* (8) is calculated taking into account the possibility of the site to site rotational energy transfer.

where v is the polarization-averaged sound velocity, ω_D is the Debye frequency [$\omega_D = (6\pi^2)^{1/3} v/a$], a is the lattice parameter, and $l(\omega)$ is the phonon mean free path, which in the case of Umklapp processes can be written as:

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

where A is a numerical coefficient. Expression (2) is inapplicable if $l(\omega)$ is of the order of or less than half the phonon wavelength $\lambda/2 = \pi v/\omega$ [6]. In a general case:

$$l(\omega) = \begin{cases} v/\alpha\omega^2 T, & 0 \leq \omega \leq \omega_0, \\ \alpha\pi v/\omega = \alpha\lambda/2, & \omega_0 < \omega \leq \omega_D, \end{cases} \quad (3)$$

where α is a numerical factor of the order of 1. The cut-off frequency ω_0 can be defined as

$$\omega_0 = 1/\alpha\pi AT. \quad (4)$$

If the mean free path of all modes exceeds $\lambda/2 = \pi v/\omega$, the thermal conductivity is determined solely by phonon scattering processes. In this case, Eq. (1) gives the well-known $\Lambda \propto 1/T$ law. If the mean free path of high-frequency modes reaches its minimum, the integral in (1) is broken into two parts describing the contributions to the heat transfer from the low-frequency phonons and high-frequency «diffusive» modes: $\Lambda = \Lambda_{\text{ph}} + \Lambda_{\text{dif}}$. In the high-temperature limit ($T \geq \Theta$) these contributions are:

$$\Lambda_{\text{ph}} = \frac{k_B \omega_0}{2\pi^2 v AT}, \quad (5)$$

$$\Lambda_{\text{dif}} = \frac{\alpha k_B}{4\pi v} (\omega_D^2 - \omega_0^2). \quad (6)$$

If all vibrational modes are scattered at distances of the order $\lambda/2$, the thermal conductivity reaches its lower limit Λ_{\min} :

$$\Lambda_{\min} = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \nu. \quad (7)$$

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 z [9]. Taking into account this property of molecular crystals, the lower limit of thermal conductivity can be represented as [8]

$$\Lambda_{\min}^* = \left(\frac{\pi}{6}\right)^{1/3} \left(1 + \frac{z}{3}\right) k_B n^{2/3} \nu. \quad (8)$$

Unfortunately, to our knowledge, no experimental data is available on the sound velocity of solid CF₂Cl₂. In this respect, the Debye temperature can be appreciated as the upper boundary frequency of translational modes from the Raman and IR absorption data [4]. Considering it to be 55 cm⁻¹ we have the calculated value of Debye sound velocity as 1250 m/s (Table 1).

Table 1. Debye model parameters of thermal conductivity used in the fitting and other quantities which were used in calculations

$a, 10^{-10}$ m	$\nu, \text{m/s}$	g	$A, 10^{-16}$ s/K	α	$\omega_D, 10^{13}$ s
4,6	1250	5.0	3.8	2.01	1.05

Fitting of the thermal conductivity using Eqs. (5),(6) 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, ω_D), and the fitted values A and α are listed in Table 1 along with the Bridgman coefficients obtained in experiment [1]. 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 Λ_{ph} and the high-frequency «diffusive» modes Λ_{dif} (calculated from Eqs. (5),(6)). The dotted line shows the lower limit of thermal conductivity Λ_{\min}^* (8) calculated taking into account a possibility of site to site rotational energy transfer. In solid CF₂Cl₂, the «diffusive» behavior of oscillatory modes starts below 80 K. As the temperature is raised the amount of heat transferred by

«diffusive» modes increases. The solid curve calculated with fitting parameters (Fig. 2) adequately describes the behavior of the temperature dependence of the isochoric thermal conductivity and agrees with the results of direct investigations of isochoric thermal conductivity [1].

3. Conclusion

This study reports measurement results of thermal conductivity in solid CF₂Cl₂. Our data are in good agreement with those results for the same condition (P, T) [1]. The isochoric experimental data [1] are discussed here with a stress on the deviations from the classical dependence $\Lambda \propto 1/T$. The reason for this deviation can be attributed to the fact that the thermal conductivity approaches its lower limit. A theoretical model where heat is transferred by phonons and above phonon cut-off frequency by «diffusive» modes is employed to test the validity of this assumption. The phonon cut-off frequency ω_0 is determined from the condition, that the phonon mean-free path restricted by the Umklapp processes cannot become smaller than half of the phonon wavelength. We conclude, that the suggested model can be applied to the simulation of the isochoric thermal conductivity in the orientationally ordered phases of molecular crystals.

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