

The thermal conductivity jump at crystal–liquid phase transition in CHCl_3 , C_6H_6 , and CCl_4 : the action of rotational molecular motion

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The thermal conductivity of liquid CHCl_3 , C_6H_6 , and CCl_4 was measured by steady-state method under saturated vapour pressure in the temperature areas that correspond to pre-crystallization temperatures. Based on the obtained experimental results, we have investigated the isobaric thermal conductivity jump $\Delta\Lambda_p$ at crystal–liquid phase transition in CHCl_3 , C_6H_6 , and CCl_4 . The contributions of the phonon–phonon and phonon–rotational interaction to the total thermal resistance, in solid and liquid state, are specified using modified method of reduced coordinates. A reduction in the thermal conductivity $\Delta\Lambda_p$ at crystal–liquid phase transition is explained by a combined effect of variations in positional distribution of molecules and in form of rotational molecular motion.

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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1. Introduction

In studies of correlation between the melting and thermophysical properties, the structural peculiarities of substances must be taken into account. It should be noted, that the varied processes tending to general increase of entropy at phase transition to liquid state are not independent of one another. A direct separation of these processes is rather complicated problem. Therefore, a simplified approach, where entropy raise processes are considered independently, is often used in practice. In this approximation the total entropy of melting can be treated as sum of components corresponding to different types of disordering processes.

Simple molecular crystals are characterized by both translational and orientational degrees of freedom. Depending on a specific crystal and temperature the form of orientational motion can vary from librations at small angles to nearly free rotation. As a result of melting, in all types of crystals the translational (positional) disordering

occurs. The orientational disordering at melting can occur, as a rule, in simple molecular crystals formed from low-symmetry molecules.

The present paper gives an account of studies of isobaric thermal conductivity jump at crystal–liquid phase transition in CHCl_3 , C_6H_6 , and CCl_4 . We focused our attention on the role of translation-orientational disordering processes at melting. To elucidate the issue, how different forms of thermal molecular motion affect the Λ_p -jump at melting, in present study the contributions of the phonon–phonon and phonon–rotational interaction to the total thermal resistance, at pre and above melting temperatures, are separated using modified method of reduced coordinates.

2. Experimental technique

The isobaric thermal conductivity of liquid CHCl_3 , C_6H_6 , and CCl_4 was measured using the steady-state method at pre-crystallization temperatures. The measure-

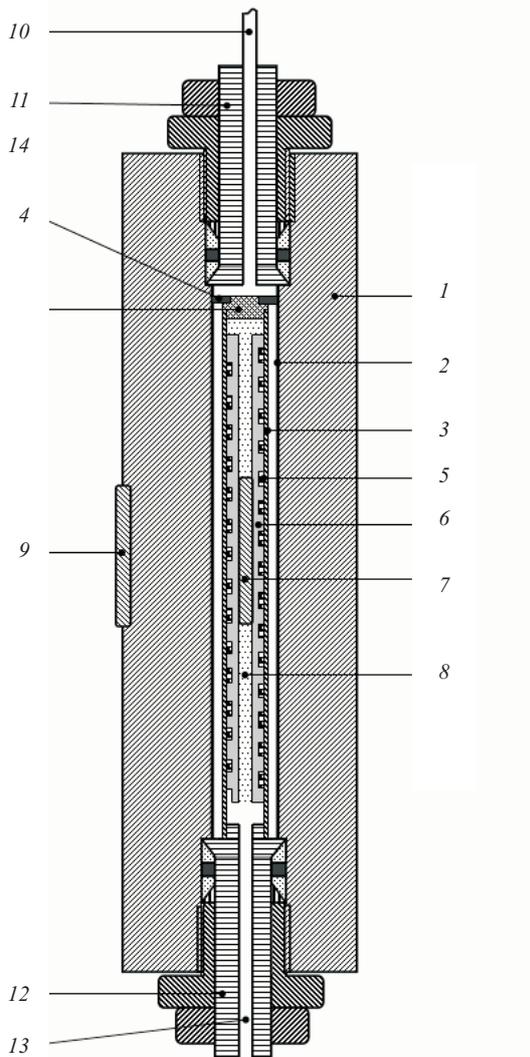


Fig. 1. The schematic of the measuring cell: 1 — external copper cylinder; 2 — stainless steel tube pressed in copper cylinder; 3 — inner cylinder; 4 — inner cylinder plug; 5 — internal heater; 6 — internal heater copper base used to equalization of the axial heat flow; 7 — internal platinum thermometer; 8 — high-heat conducting powder; 9 — external platinum thermometer; 10 — channel of substance pressure feed; 11, 12 — bridgman seals; 13 — service duct; 14 — fluoroplastic centering ring.

ments were carried out on coaxial-geometry setup (Fig. 1) under atmospheric pressure. The measurement cell was produced from copper, with a length of 175 mm and an inside diameter of 11 mm, which made it possible to eliminate the axial heat flow. The inner measuring cylinder was 10 mm in diameter and produced from stainless steel. The liquid samples were between the outer and the inner cylinder. The temperature sensors were platinum resistance thermometers, which were mounted on the surface of measuring cell and in the channel of the inner cylinder. The heat fluxes due to thermal radiation were reduced substantially with the aid of a radiation shield, on which the temperature field of the measuring cell was reproduced. The measurements were made on the two samples

of each substance of 99.9% purity; the uncertainty in thermal conductivity measurement did not exceed 3%.

3. Results and discussion

Figure 2 shows the experimental results for three substances. The Λ_p of liquid CHCl_3 , C_6H_6 and CCl_4 decreases with temperature rises. The Λ_p -data for solid CHCl_3 , C_6H_6 and CCl_4 , at pre-melting temperatures (Fig. 2), were taken from [1]. The thermal conductivity jump was calculated at pre and above melting temperatures as $\Delta\Lambda = \Lambda_{\text{solid}} - \Lambda_{\text{liquid}}$. The Λ_p -jump at phase transition essentially depends on the substance. Our results show that:

$$\Delta\Lambda_{\text{CCl}_4} = 0.007 \text{ W / (m}\cdot\text{K)},$$

$$\Delta\Lambda_{\text{C}_6\text{H}_6} = 0.103 \text{ W / (m}\cdot\text{K)},$$

$$\Delta\Lambda_{\text{CHCl}_3} = 0.11 \text{ W / (m}\cdot\text{K)}.$$

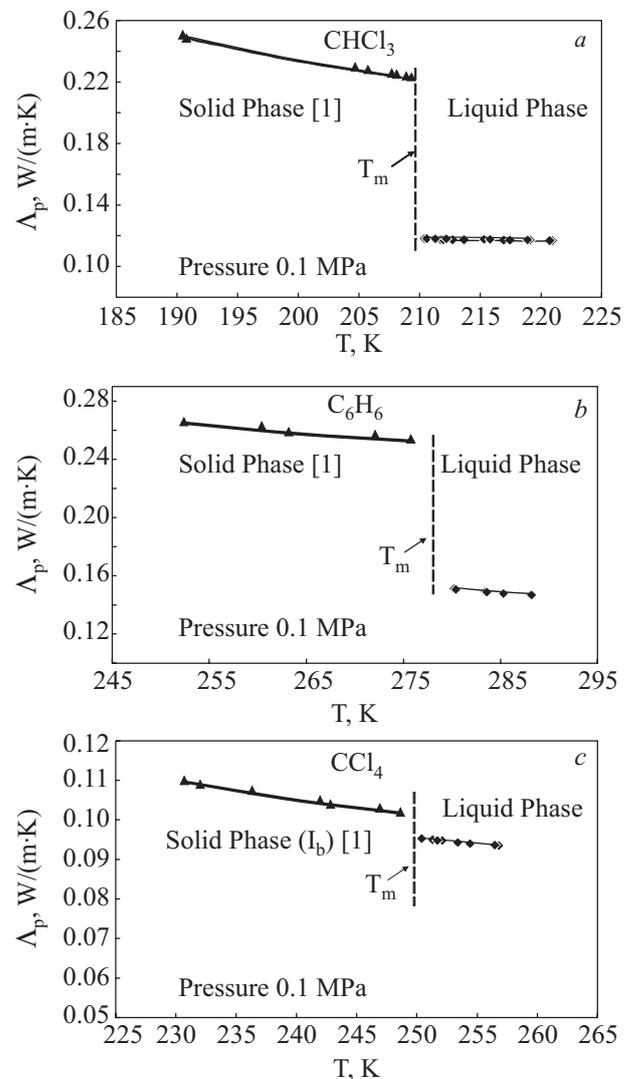


Fig. 2. T -dependence of isobaric thermal conductivity Λ_p in solid [1] and liquid CHCl_3 (a), C_6H_6 (b), and CCl_4 (c) at crystal-liquid phase transition. T_m is the melting temperature.

A reduction (Fig. 2) in the thermal conductivity at crystal–liquid phase transition is usually connected with jump-like volume changes resulting from variation in the positional distribution of molecules and variations in the rotational molecular motion.

At pre-melting temperatures investigated substances differ essentially in nature of rotational molecular motion. Chloroform remains to be orientationally ordered until the melting temperature is reached [2] (the reorientation frequencies do not exceed 10^4 s^{-1} , and entropy of melting is $\Delta S_f/R = 5.4$). In solid benzene the melting-caused change in the entropy of melting is $\Delta S_f/R = 4.22$, which is much larger than Timmermans criterion for orientationally disordered phases. The frequency of molecular reorientations at 85 K is 10^4 s^{-1} [3]. On a further rise of temperature it increases considerably, reaching 10^{11} s^{-1} near melting temperature. The basic frequency of the benzene molecule oscillations about sixfold axis at 273 K is $1.05 \cdot 10^{12} \text{ s}^{-1}$ [4]. It is clear from these data that solid benzene is a crystal where, provided that the temperature grows, the transition from libration of molecules to hindered rotation takes place only about one axis, or in other words solid C_6H_6 is partially disordered crystal. Because of low entropy of melting $\Delta S_f/R = 1.21$ [3], the high-temperature phase of carbon tetrachloride may be classified as plastic. According to experimental data [5], the character of the molecular motion in the plastic phase of CCl_4 is close to that in liquid state.

To understand of how different forms of thermal molecular motion affect the Λ_p -jump at crystal–liquid phase transition the contributions of the phonon–phonon and phonon–rotational interaction to the total thermal resistance, in solid and liquid state, are separated using modified method of reduced coordinates [1]. Under the assumption that the contributions of the phonon–phonon W_{pp} and phonon–rotation W_{pr} interactions to the total thermal resistance $W_p = 1/\Lambda_p$ are additive, we separate the phonon–rotation component. It is important to note that, in this case, there is no necessity to engage that or another approximate model of heat transfer. Suggesting that the thermal resistance of molecular crystals resulting from phonon–phonon scattering W_{pp} , when being expressed in terms of reduced coordinates ($W^* = W/W_{\text{mol}}$, $T^* = T/T_{\text{mol}}$), is identical to that for solidified inert gases at the same reduced volume $V^* = V/V_{\text{mol}}$, one can extract the phonon–phonon W_{pp} , and phonon–rotational W_{pr} components of the thermal resistance. As a rule, the reduction parameters are $T_{\text{mol}} = \epsilon/k_B$, $\Lambda_{\text{mol}} = k_B / \sigma^2 \sqrt{\epsilon/\mu}$, and $V_{\text{mol}} = N\sigma^3$, where σ and ϵ are the parameters of Lennard–Jones potential, μ is the molar weight, and N is the total number of particles.

Here, we used the temperatures T_{cr} and the molar volumes V_{cr} of CHCl_3 , C_6H_6 , and CCl_4 and the solidified inert gases Kr and Xe at their critical points [6] as the reduc-

tion parameters T_{mol} and V_{mol} (see Table 1). Such a choice of critical coordinates is explained by the fact that, in the case of simple molecular substances, the critical parameters T_{cr} and V_{cr} are proportional to ϵ and σ^3 , respectively. However, the determination accuracy of critical parameters is much higher than the accuracy of binomial potential parameters.

Table 1. Reduction parameters and molar weights for Kr, Xe, CHCl_3 , C_6H_6 , and CCl_4

Substance	T_{cr} , K	V_{cr} , cm^3/mole	μ , g/mole	W_{mol} , (m·K)/W
Kr	209.4	92.01	83.8	8.06
Xe	289.7	119.4	131.3	10
CHCl_3	536.6	238.8	119.4	10.9
C_6H_6	562	260	78	9.43
CCl_4	556.4	257	153.8	13.2

Figure 3 shows the results of our thermal resistance components calculations. In all cases, the values of phonon–phonon component W_{pp} at pre-crystallization temperatures exceed the corresponding values of W_{pp} at pre-melting temperatures. The distinctions ΔW_{pp} of phonon–phonon thermal resistance in liquid and solid state are proportional to variations in positional distribution of the molecules resulting from melting. The values of phonon–rotational thermal resistance W_{pr} in CHCl_3 and C_6H_6 at pre-crystallization temperatures are more than respective values W_{pr} at pre-melting temperatures. The enhancement ΔW_{pr} of phonon–rotational components can be attributed to additional scattering of phonons on collective rotational excitations, the density of which increases resulting from intense growth of the processes of orientational disordering at crystal–liquid phase transition; so that ΔW_{pr} is proportional to growth of orientational disordering processes at melting. In the case of CCl_4 , the phonon–rotational thermal resistance decreases at phase transition in liquid state. In our opinion, the later results from the disappearance of the correlation in orientational molecular motion and transition of the CCl_4 -molecules to hindered rotation. This is in good agreement with the data cited in [5] indicating that the character of the molecular motion in CCl_4 at pre-melting temperatures is close to that in liquid state. It is interesting to compare the relationship between W_{pp} and W_{pr} in solid and liquid zone of melting. At pre-melting temperatures, the phonon–rotational thermal resistance W_{pr} comprises 55% for CHCl_3 , 5% for C_6H_6 and 50% for CCl_4 of the phonon–phonon thermal resistance W_{pp} . As a conse-

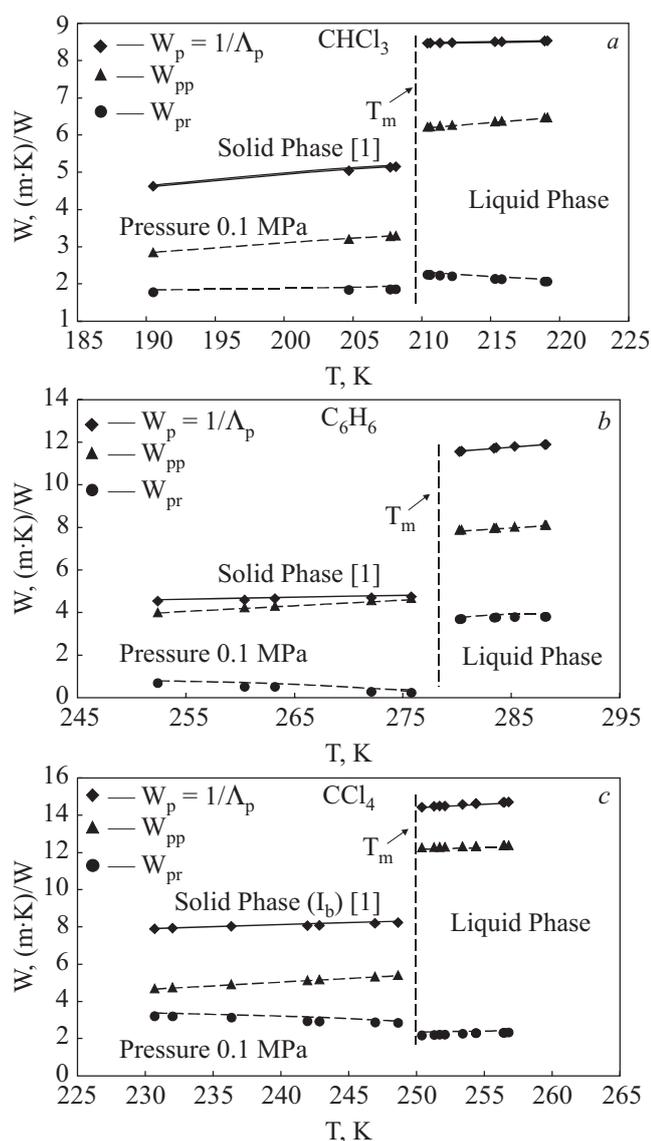


Fig. 3. Phonon–phonon W_{pp} and phonon–rotational W_{pr} components of the total thermal resistance W in CHCl_3 (a), C_6H_6 (b), and CCl_4 (c), calculated for the solid and liquid phases. The solid line shows the sum of thermal resistances W_{pp} and W_{pr} .

quence of melting, the change in magnitude of relationship between W_{pp} and W_{pr} occurs, and at pre-crystalliza-

tion temperatures, phonon–rotational thermal resistance comprises 35% for CHCl_3 , 45% for C_6H_6 , and 17% for CCl_4 of the phonon–phonon thermal resistance.

4. Conclusion

The isobaric thermal conductivity jump at crystal–liquid phase transition has been investigated in CHCl_3 , C_6H_6 and CCl_4 . It is shown that the reduction in the thermal conductivity $\Delta\Lambda_p$ at melting derives from the combined effect of variations in positional distribution of molecules and in the form of rotational molecular motion. It was found that the melting of investigated crystals involves an increase of phonon–phonon thermal resistance due to the disordering processes in translational subsystem. The action of rotational molecular motion at melting is dissimilar depending on the substance. For example, in orientationally-ordered crystalline CHCl_3 and partially orientationally-disordered crystalline C_6H_6 , as a result of melting, the increase of phonon–rotational thermal resistance occurs, whereas in orientationally-disordered crystalline CCl_4 during the process of melting one observes the decrease of phonon–rotational thermal resistance. The reason is the disappearance of the correlation in orientational molecular motion and transition of CCl_4 -molecules to localized hindered rotation accompanied by the negative jump of orientational entropy at melting.

1. O.I. Pursky, N.N. Zholonko, and V.A. Konstantinov, *Fiz. Nizk. Temp.* **29**, 1021 (2003) [*Low Temp. Phys.* **29**, 771 (2003)].
2. H.S. Gytowsky and D.N. McCall, *J. Chem. Phys.* **32**, 548 (1966).
3. A.R. Ubbelohde, *Melting and Crystal Structure*, Clarendon Press, Oxford (1965).
4. N.G. Parsonage and L.A.K. Staveley, *Disorder in Crystals*, Clarendon Press, Oxford (1978).
5. D.E. O'Reilly, E.M. Peterson, and C.R. Scheie, *J. Chem. Phys.* **60**, 1603 (1974).
6. *Table of Physical Values. Reference Book*, I.K. Kikoin (ed.), Atomizdat, Moscow (1976) (in Russian).