

# The isochoric thermal conductivity of solid $n$ -alkanes: propane $C_3H_8$

V.A. Konstantinov, V.P. Revyakin, and V.V. Sagan

*B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine  
47 Lenin Ave., Kharkov 61103, Ukraine  
E-mail: konstantinov@ilt.kharkov.ua*

Received March 20, 2009

The isochoric thermal conductivity of solid propane  $C_3H_8$  has been investigated on three samples of different densities in the temperature interval from 50 K to the onset of melting. In all the cases the isochoric thermal conductivity exhibits dependences that are weaker than  $\Lambda \propto 1/T$ . The results obtained are compared with those for other representatives of  $n$ -alkanes. The experimental data are discussed within a model in which the heat is transported by low-frequency phonons and by «diffusive» modes above the phonon mobility edge.

PACS: **66.70.-f** Nonelectronic thermal conduction and heat-pulse propagation in solids; thermal waves;  
**63.20. K**– Phonon interactions.

Keywords: isochoric thermal conductivity, phonons, diffusive modes, solid propane.

Normal alkanes  $C_nH_{2n+2}$  form a class of substances taking an intermediate, transitional position between simple molecular solids and long-chain polymers which attracts considerable interest. The  $n$ -alkanes have a deceptively simple composition and a molecular packing in the solid state: the lamellae of molecules are aligned as chains parallel to one another and nearly perpendicular to the lamella plane. Yet, despite this seeming simplicity, they show an extraordinary variety of dynamical behavior both in the solid and liquid states. There is an intriguing «odd-even» effect alternating the orthorhombic versus triclinic unit cells between the adjacent members of the series as well as the presence or absence of premelting rotator phases. Glassy crystalline «rotator phases» with a hexagonal symmetry are found below the melting points of the odd-numbered  $n$ -alkanes starting with  $n = 9$ . The difference between the phase transition and melting points increases with the chain length. The hexagonal modifications are also observed for the even-numbered  $n$ -alkanes starting with  $n = 22$  [1,2]. The nature of the molecular disorder in the «rotator phases» of  $n$ -alkanes is not fully clear. Besides the more or less hindered rotation of the molecules about the long axes other additional forms of disorder have been discussed [3]. The melting point alternation is another well-known phenomenon in  $n$ -alkanes; that is, the even-numbered members of series melt at a relatively higher temperature than the odd-numbered members [1].

The short-chain ( $n < 6$ )  $n$ -alkanes are the least known members of the series. Previously, we studied the isochoric thermal conductivity of methane [4] and ethane [5]. Here we explore studies of the heat transfer in saturated hydrocarbons further. The isochoric thermal conductivity of solid propane  $C_3H_8$  was studied on samples of different densities in the temperature interval from 50 K to the onset of melting. Constant-volume investigations are possible for molecular solids having comparatively high compressibility coefficients. Using a high pressure cell, it is possible to grow samples of sufficient density which can be cooled then with practically invariable volume whereas the pressure in the cell decreases. As samples of moderate densities are cooled the pressure in the cell drops to zero at a certain characteristic temperature  $T_0$  and the isochoric condition is then broken. On further cooling, the sample can separate from the walls of the cell or its continuity can be disturbed. In constant-volume experiments melting and solid-solid phase transitions occur in a certain temperature interval, and their onset shifts towards higher temperatures as the density of the samples increases.

The reported measurements were made by a stationary method on a coaxial geometry device [6]. The samples were grown at pressures from 40 MPa to 120 MPa at the temperature gradient along the measuring cell being about 1.5 K/cm. When the growth was completed, the capillary was blocked by freezing it with liquid hydrogen,

and the samples were annealed for one to two hours at  $\sim 80$  K to remove the density gradients. After the measurements, the samples were evaporated into a thin-walled vessel and their masses were measured by weighing. The molar volumes of the samples were found from the known volume of the measuring cell and the sample masses. The purity of  $C_3H_8$  was no worse than 99.85%.

The melting point of propane is the lowest among *n*-alkanes ( $T_m = 85.45$  K) the melting entropy being  $\Delta S_f/R = 4.96$  [7]. According to heat capacity data [7], there are no phase transitions in the interval 13–85 K. The potential barrier for internal rotation (rotation of the methyl groups about the  $C_3$ -axis) is 13.8 kJ/mole [8,9]. In more recent studies of the triple point of propane, two solid phases were detected, one stable, the other metastable [10]. The triple-point temperature of the stable solid is  $(85.520 \pm 0.003)$  K and the enthalpy of fusion is  $(3.50 \pm 0.025)$  kJ/mole. The metastable phase reaches the triple-point temperature at  $(81.226 \pm 0.003)$  K and its enthalpy of fusion is  $(2.4 \pm 0.3)$  kJ/mole. On freezing below 79.6 K, the stable phase is only observed, the transition between the two solid phases occurs in the range 79.6 to 81.2 K; the enthalpy of the metastable — stable transition is  $(0.70 \pm 0.03)$  kJ/mole. As soon as the stable phase is formed, it is almost impossible to obtain the metastable form again from the remelted liquid without returning to room temperature.

The crystal structure of propane ( $P2_1/n, Z = 4$ ) was determined at 30 K by the x-ray technique [1]. It consists of layers of molecules in successive  $(\bar{1}01)$  planes. The adjacent layers are at a typical close-packing separation of 3.60 Å. The layers in the structure of propane are not perfectly flat, they are slightly corrugated because the molecular plane is slightly inclined ( $10^\circ$ ) with respect to the layer plane. One may expect that the rotation about the long axis in *n*-alkanes is accompanied by a translation along the axis [2].

The experimental results are shown in Fig. 1 (solid lines are smoothed thermal conductivity values of the solid phase). The isochoric thermal conductivity of the three samples decreases with rising temperature by the law weaker than  $\Lambda \propto 1/T$ , has a bend and then decreases more rapidly. The bend can be associated with the onset of the sample melting. Two phases solid and liquid coexist above it; the amount of the liquid phase increases with temperature. The thermal conductivity of liquid propane at atmosphere pressure is shown at the bottom right according to data [11]. Arrows mark the onset of the constant-volume condition ( $T_0$ ) and the onset of the sample melting ( $T_m$ ). We consider that the probability of the formation of the metastable phase at premelting temperatures is insignificant in our experiment (see [10]). The thermal conductivities of samples grown under the same conditions (pressure, time and temperature gradient along the measuring cell) coincide within the experimental er-

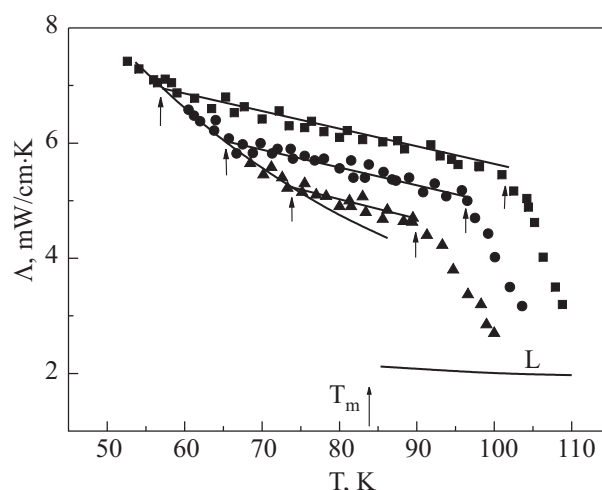


Fig. 1. The isochoric thermal conductivity of three solid propane samples ( $C_3H_8$ ) of different densities: No 1 (▲), No 2 (●), No 3 (■) (see also Table 1). Solid lines show smoothed values of isochoric thermal conductivity. The thermal conductivity of liquid propane at the atmospheric pressure is shown at the bottom right according to data [11]. Arrows mark the onset of the experimental condition  $V = \text{const}$  and the onset of the sample melting.

ror, thus suggesting that the samples were fine-dispersed (one can expect of significant anisotropy of the thermal conductivity along and across of lamella plane).

The molar volumes of the samples  $V_m$ , the temperatures  $T_0$  (onset of  $V = \text{const}$  condition) and  $T_m$  (onset of melting) are also shown in Table 1. The Bridgman coefficient  $g = -(\partial \ln \Lambda / \partial \ln V)_T$  calculated from the experimental data is  $7.5 \pm 0.8$  at  $T = 85$  K. Monotonic decrease of thermal conductivity was also observed in the solid odd-numbered *n*-alkanes ranging from  $C_9H_{20}$  to  $C_{19}H_{40}$  [12] and in the low temperature phase of ethane [5]. An important feature of the odd-numbered *n*-alkanes exhibiting a plastic crystal phase is a considerable jump in the thermal conductivity at the liquid  $\rightarrow$  plastic phase transition and the subsequent transition from the plastic to the ordered phase [12]. The total jump  $\Delta\Lambda/\Lambda_L$  between liquid and ordered phase is 120–130% for the odd-numbered *n*-alkanes ( $n = 9$ –19) and 110% for propane. It is much larger than for the globular-shaped molecules [13], in particular,  $\Delta\Lambda/\Lambda_L$  is only 20–30% for methane and ethane [4,5]. This may correlate with the much higher degree of orientational ordering in solid chain-shaped *n*-alkanes in contrast to solids formed by the globular-shaped molecules. We estimated the molar volume of solid propane to be  $58.1 \text{ cm}^3/\text{mole}$  at the triple-point temperature. Stewart and Rock have a lower value  $57.8 \text{ cm}^3/\text{mole}$  at 77 K [14]. The molar volume of the liquid propane is  $60.1 \text{ cm}^3/\text{mole}$  at the triple-point temperature [11]. Thus the change in the volume during melting is near 3.5%, which is the lowest value obtained for *n*-alkanes [15].

Table 1. Molar volumes  $V_m$  of samples, temperatures  $T_0$  of the onset of experimental condition  $V = \text{const}$  and temperatures  $T_m$  of the onset of melting

Number of sample	$V_m$ , cm <sup>3</sup> /mole	$T_0$ , K	$T_m$ , K
1	56.4	59	102
2	57.0	67	94
3	57.6	76	88

As was shown earlier, the deviations of the isochoric thermal conductivity from the dependence  $\Lambda \propto 1/T$  in the orientationally — ordered phases of molecular crystals can be explained proceeding from the concept of «lower limit to thermal conductivity» [16,17]. In this case the thermal conductivity can be calculated using a model in which heat is transported by low-frequency phonons or by «diffusive» modes above the mobility edge. Let us express the thermal conductivity as

$$\Lambda(T) = 3nk_B v \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} l(x) \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where  $\Theta_D = v(h/2\pi k_B)(6\pi^2 n)^{1/3}$ ,  $n$  is the number of atoms (molecules) per unit volume,  $v$  is the sound velocity averaged over polarizations, and  $l(x)$  is the mean free path of the phonons. For  $T \geq \Theta_D$  the mean free path is governed mainly by the umklapp processes:

$$l(x) = \frac{1}{CT} \frac{h^2 v^2}{k_B^2 T^2 x^2}, \quad (2)$$

where  $C$  is a coefficient. Since the mean free path of the phonons cannot be shorter than the half wavelength  $l(x) = \alpha\lambda/2$ , where  $\alpha \approx 1$ , the «diffusivity edge»  $\Theta_*$  is

$$\Theta_* = 2hv/\alpha k_B CT. \quad (3)$$

«Diffusive» refers to the modes whose mean free path is  $\alpha\lambda/2$ . We assume that  $\Theta_* \leq \Theta_D$ , otherwise  $\Theta_* = \Theta_D$ . The integral of the thermal conductivity can be decomposed into two parts, describing the contribution to the thermal conductivity from the low — frequency phonons and the high — frequency «diffusive» modes:

$$\Lambda = \Lambda_{\text{ph}} + \Lambda_{\text{dif}}, \quad (4)$$

$$\Lambda_{\text{ph}}(T) = 3nk_B v \left( \frac{T}{\Theta_D} \right)^3 \left[ \int_0^{\Theta_*/T} l(x) \cdot \frac{x^4 e^x}{(e^x - 1)^2} dx \right], \quad (5)$$

$$\Lambda_{\text{dif}}(T) = 3nk_B v \left( \frac{T}{\Theta_D} \right)^3 \left[ \int_{\Theta_*/T}^{\Theta_D/T} \alpha \frac{vh}{2k_B x T} \cdot \frac{x^4 e^x}{(e^x - 1)^2} dx \right]. \quad (6)$$

A computer least-squares fit with smoothed values of the thermal conductivity was performed for the most dense sample with  $V_m = 56.4$  cm<sup>3</sup>/mole. Unfortunately, there are no data about the sound velocity in solid propane. Therefore, three parameters  $C$ ,  $v$  and  $\alpha$  were varied. The best agreement with experiment was obtained for  $C = 1.1 \cdot 10^{-9}$  cm/K,  $v = 1.95 \cdot 10^5$  cm/s, and  $\alpha = 2.84$ . For comparison, the sound velocity in liquid propane is  $2.17 \cdot 10^5$  cm/s at 85.5 K [11]. The coefficients  $C$  and  $\alpha$  are close to values observed in the other orientationally ordered phases of molecular crystals [17].

Figure 2 shows the smoothed values of the measured thermal conductivity, the fitted curve and the contributions of the low — frequency phonons  $\Lambda_{\text{ph}}$  and the «diffusive» modes  $\Lambda_{\text{dif}}$  calculated by Eqs. (4)–(6). It is seen that the «diffusive» behavior of the vibrational modes begins manifest itself above 40 K, at  $T > 90$  K the heat is transported mainly by the «diffusive» modes.

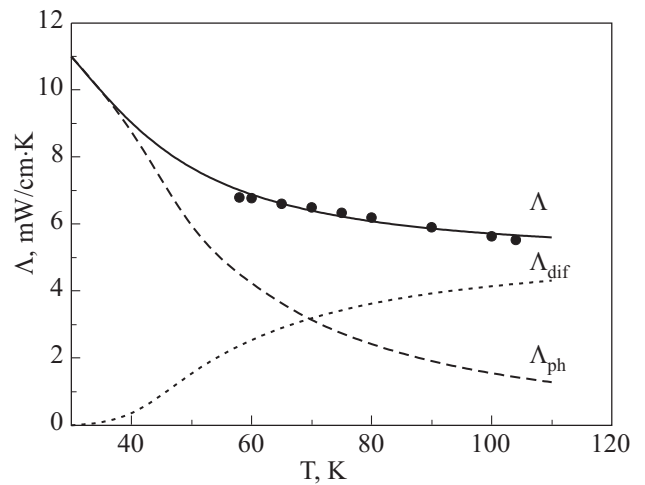


Fig. 2. The smoothed values of the measured thermal conductivity for C<sub>3</sub>H<sub>8</sub>, the fitted curve and the contributions of the low-frequency phonons  $\Lambda_{\text{ph}}$  and the «diffusive» modes  $\Lambda_{\text{dif}}$  calculated by Eqs. (4)–(6).

1. R. Boese, H. C. Weiss, and D. Blaser, *Angew. Chem. Int. Ed.* **38**, 988 (1999).
2. A. Marbeuf and R. Brown, *J. Chem. Phys.* **124**, 054901 (2006).
3. M. Maroncelli, H.L. Strauss, and R.G. Snyder, *Chem. Phys.* **82**, 2811 (1985).
4. V.A. Konstantinov, V.G. Manzhelii, V.P. Revyakin, and S.A. Smirnov, *Physica* **B262**, 421 (1999).

5. V.A. Konstantinov, V.P. Revyakin, and V.V. Sagan, *Fiz. Nizk. Temp.* **32**, 905 (2006) [*Low Temp. Phys.* **32**, 689 (2006)].
6. V.A. Konstantinov, S.A. Smirnov, and V.P. Revyakin, *Instr. Exp. Tech.* **42**, 133 (1999).
7. J.D. Kemp and C.J. Egen, *J. Am. Chem. Soc.* **60**, 1521 (1938).
8. D.M. Grant, R.J. Pugmire, and R.C. Livingston, *J. Chem. Phys.* **52**, 4424 (1970).
9. J.A. Ripmeester, S.K. Garg, and D.W. Davidson, *J. Chem. Phys.* **67**, 2275 (1977).
10. F. Pavese and L.M. Besley, *J. Chem. Thermodynamics* **13**, 1095 (1981).
11. B.A. Younglove and J.F. Ely, *J. Phys. Chem. Ref. Data* **16**, 577 (1987).
12. H. Forsman and P. Andersson, *J. Chem. Phys.* **80**, 2804 (1984).
13. R.G. Ross, P. Andersson, B. Sundqvist, and G. Backstrom, *Rep. Prog. Phys.* **47**, 1347 (1984).
14. J. W. Stewart and R.I. La Rock, *J. Chem. Phys.* **28**, 425 (1958).
15. A.R. Ubbelohde, *Melting and Crystal Structure*, Clarendon Press, Oxford (1965).
16. D.G. Cahill, S.K. Watson, and R.O. Pohl, *Phys. Rev.* **B46**, 6131 (1992).
17. V.A. Konstantinov, *Fiz. Nizk. Temp.* **29**, 567 (2003) [*Low Temp. Phys.* **29**, 422 (2003)].