ISOBARIC THERMAL CONDUCTIVITY OF CRYSTALLINE ETHANE (C_2H_6)

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The isobaric thermal conductivity of solid C_2H_6 is measured in the temperature interval from 80 K to the melting point. The conductivity is found to decrease with the temperature growth, and its reduction at the $\beta \rightarrow \gamma$ phase transition is found to be 0.08 W/(m·K). The influence of the methyl-group (CH_3) rotation on the heat conductivity is studied in the framework of the modified method of reduced coordinates, by separating the translation and translation-rotation contributions to the total thermal resistance.

1. Introduction

Heat transfer in simple molecular crystals at temperatures of the order of the Debye temperature and above is governed by the following factors: translation and translation-orientation interactions (TOI), the approach of heat conductivity to its lower limit, and the influence of thermal expansion (TE) [1–4]. The approach of heat conductivity to its lower limit is associated with a restriction of the minimal mean free path of phonons by a distance of the order of a wavelength [5]. Such a restriction manifests itself in the range of premelting temperatures of orientationally ordered molecular crystals as the temperature dependence of heat conductivity much weaker that $1/T$ [3, 6, 7]. The dependence of heat conductivity on thermal expansion can be observed making a mutual analysis of the data obtained in isochoric and isobaric experiments. The influence of thermal expansion on heat-transfer processes was studied theoretically only in work [4], on the basis of orientationally disordered phases of simple molecular crystals. The results obtained in that work demonstrate that the thermal expansion in the orientationally disordered phases of molecular crystals gives rise to an increase of thermal resistance, which is stimulated by both phonon-phonon scattering and a reduction of thermal resistance connected with TOI due to a decrease of the potential barrier hampering the rotation of molecules.

The TOI specificity is determined by the temperature and the character of intermolecular interaction forces.

In the general case, the transition of molecules from low-amplitude librations to hindered rotation is accompanied by an increase of isochoric heat conductivity [2]. This phenomenon occurs owing to a reduction of phonon scattering by orientational vibrations of molecules. In the isobaric case, the reduction of phonon scattering due to TOI is compensated by thermal expansion, so that the isobaric heat conductivity decreases with the temperature growth, by following the dependences close to the $1/T$-law [2, 4]. The influence of TOI on heat transfer processes in molecular crystals, in which the enhancement of disordering processes – at a constant pressure – is associated with the rotational motion of molecules or molecular segments around one of the chosen axes, has not been almost studied.

In this work, the measurements of the isobaric heat conductivity coefficient of solid ethane C_2H_6—a crystal, in which the growth of orientational disorder takes place owing to the enhancement of reorientational motion of methyl groups CH_3 around the C–C axis—were carried out. The influence of TOI on heat transfer processes in crystalline C_2H_6 is studied in the framework of the modified method of reduced coordinates [8].

2. Subject under Study

Crystalline ethane C_2H_6 consists of quasilinear molecules formed by the coupling of two methyl groups CH_3 by means of the C–C bond. Besides the rotational motion of an ethane molecule as a whole, the internal rotations of methyl groups around the molecular axis C_3 are inherent to it. The results of X-ray diffraction researches presented in work [9] show that solid ethane has three crystal modifications, one of which is metastable.

The low-temperature α-phase has a monoclinic lattice with spatial symmetry $P2_1/n$ and two molecules in the elementary cell [10]. The molecules in the lattice are characterized by point symmetry D_3, the lengths of intramolecular C–C and C–H bonds are 1.532 and 1.096 Å, respectively, and the angles between C–C–H and H–C–

H bonds are 111.5 and 107.4°, respectively. The potential barrier, which interferes with the internal rotation of methyl groups around the molecular axis C_3, amounts to 12.18 kJ/mol [11].

The region, where the low-temperature α-phase exists, terminates by a phase transition into an intermediate β-phase at the temperature $T_{\alpha \to \beta} = 89.73$ K [12]. According to the results of work [9], the β-phase has an orthorhombic structure with the elementary cell parameters $a = 4.289$ Å, $b = 5.660$ Å, and $c = 5.865$ Å. The volume variation ΔV at this phase transition is 0.21 cm^3/mol, i.e. only 0.5%. The β-phase has the molar volume $V_{\mathrm{mol}} = 42.88$ cm^3/mol and the density of 0.6996 g/cm^3 at such parameters.

An interesting feature of the β-phase is that the monoclinic α-phase always transforms at heating into the orthorhombic β-phase which, in turn, transforms into the γ-modification, if heating is continued further. However, when the γ-phase is cooled down, the α-phase is always obtained, i.e. the orthorhombic β-phase does not emerge, if the temperature is reduced. Proceeding from this fact, the authors of work [9] considered the intermediate orthorhombic β-phase as a metastable one.

The high-temperature $\beta \to \gamma$ phase transition occurs at the temperature $T_{\beta \to \gamma} = 89.83$ K [12]. The corresponding entropy variation is $\Delta S_{\beta \to \gamma}/R = 3.065$ [13], and the corresponding relative variation of the volume amounts to 6.8%. The high-temperature γ-phase of C$_2$H$_6$ was found to have a body-centered cubic (bcc) lattice characterized by the parameter $a = 5.304$ Å. The spatial symmetry group of the high-temperature γ-phase is $Im3m$, with two molecules in the elementary cell which are oriented by the C–C axis along the spatial diagonals $\langle 111 \rangle$ of the cube. The high-temperature phase density determined from X-ray researches is 0.699 g/cm^3 at $T = 90$ K. When crystalline C$_2$H$_6$ melts, a step-like variation of the volume by 2% occurs at the temperature $T_m = 90.35$ K [10]. The low entropy of the melting of solid C$_2$H$_6$ $\Delta S_m/R = 0.78$ [13] allows the high-temperature γ-phase to be classed as a plastic one.

Hence, the structural phase transitions in solid ethane occur at temperatures above 89.6 K, i.e. in the vicinity of its melting point. The most radical is the $\beta \to \gamma$ transition. The total volume variation in the temperature interval $5-90$ K is 5.11 cm^3/mol or 12.5%, with the largest contribution to this variation given by the phase transition into the bcc phase (6.8%). The enthalpy of the $\beta \to \gamma$ transition is almost 25 times larger than that of the $\alpha \to \beta$ transition. The jump-like change of the volume is 10 times larger, and it is accompanied by substantial variations of the lattice symmetry and the orientational structure of the crystal [9].

The analysis of the spin relaxation time, which was carried out in work [12], showed that the characters of orientational molecular motion in three phases of solid C$_2$H$_6$ are essentially different. In the monoclinic phase, the orientational motion of molecules is reduced to their 120°-reorientations around the molecular axis C_3. At the same time, molecular reorientations around this axis become impossible in the intermediate β-phase. The authors of work [12] arrived at a conclusion that there are two orientationally ordered phases in solid ethane at $P = 0$. In the high-temperature, orientationally disordered phase, the translational diffusion becomes a governing process for spin-lattice relaxation, molecular reorientations occur around different axes, and the disorder gets a dynamic character.

A similar conclusion with respect to the bcc phase was drawn by the authors of work [9] on the basis of researches of the temperature behavior of the lattice volume and parameters. When the temperature approaches the point of the phase transition into the γ-phase, a substantial anisotropy of thermal expansion was observed. This anisotropy is associated with the enhancement of rotational processes around the C–C axis and with increase in the amplitude and the frequency of librations of C$_2$H$_6$ molecules with respect to the second-order axes.

Till now, only the isochoric heat conductivity of solid C$_2$H$_6$ in the temperature range from 35 K to the melting temperature has been studied [14].

3. Results and Their Discussion

The isobaric heat conductivity of solid ethane was studied using the linear-flow stationary method [15] in the temperature range from 80 K to the melting temperature. Measurements were carried out for two free specimens, under the pressure of their own saturated vapors. Polycrystalline specimens were grown up from the gas phase, under a pressure of 1.4 atm. The temperature of the measuring ampoule bottom was maintained to be close to the liquid nitrogen temperature of 80 K. The purity degree of the gas under investigation was not worse than 99.96%. The total systematic error of the experiment did not exceed 5%.

The results of the experiment are presented in Fig. 1,a. Within the experiment error limits, the heat conductivities of two specimens coincide. The isobaric heat conductivity decreases with the temperature growth. In the α-phase, it falls down, by following the dependence $\Lambda_p \propto T^{-1.6}$. A minor variation of the volume (0.5%) at
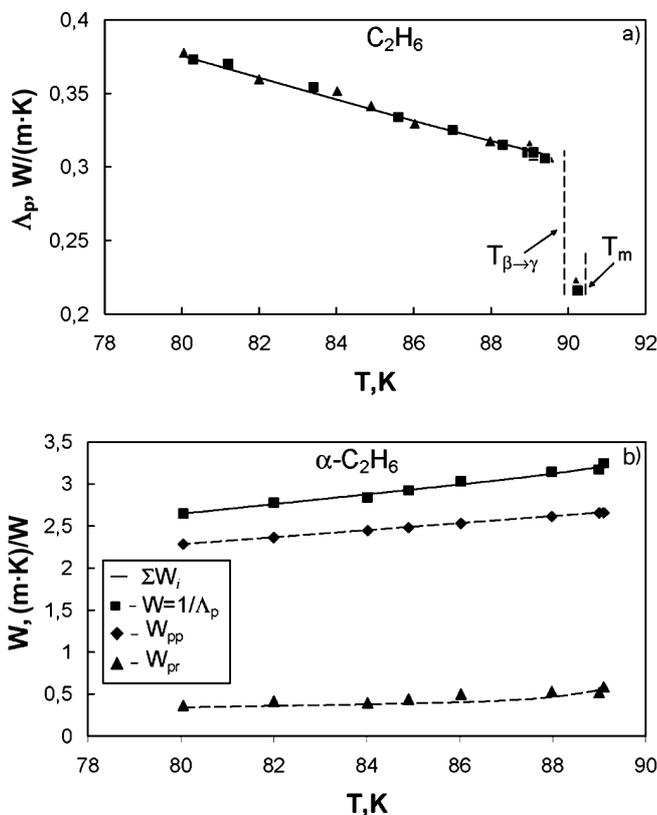
(*a*) Temperature dependence of the heat conductivity of solid C_2H_6. The solid curve corresponds to smoothed experimental data on the isobaric heat conductivity. $T_{\beta \rightarrow \gamma}$ is the temperature of phase transition into the plastic phase, and T_m is the melting temperature. (*b*) Contributions connected with the phonon-phonon, W_{pp}, and phonon-rotational, W_{pr}, scattering to the total thermal resistance $W = 1/\Lambda$. ΣW_i is the sum of W_{pp} and W_{pr}

the $\alpha \rightarrow \beta$ phase transition induces variations in the heat conductivity, but those variations are much less than the experimental error. Therefore, no influence of the phase transition into the orthorhombic phase on the heat conductivity has been registered experimentally. Considerable changes of the heat conductivity occur at the $\beta \rightarrow \gamma$ phase transition. After the transition, the volume increases by almost 7%, which leads to a reduction of the heat conductivity by 0.08 W/(m×K).

Among all studied crystals, solid ethane has a plastic phase with the lowest temperature range of existence [13]. Therefore, the heat conductivity coefficient in the γ-phase was actually measured at a single temperature of 90.22 ± 0.02 K. In connection with this circumstance, we cannot discuss the temperature dependence of C_2H_6 isobaric heat conductivity in the plastic phase.

In this work, the influence of the reorientational motion of methyl groups CH_3 on heat transfer processes in the α-phase of C_2H_6 is studied taking advantage of the modified method of reduced coordinates, by separating the contributions of the translation and translation-orientation interactions to the total thermal resistance. The technique of calculations in the framework of the given method was described in works [2, 8]. At calculations, we used values of the temperature and the molar volume of Xe and C_2H_6 at the corresponding critical points [17] (see Table), the temperature dependences of the molar volume for C_2H_6 and Xe [9, 16, 18], and the isobaric heat conductivity data for Xe [19].

The calculation results for components of the total thermal resistance W in the α-phase of C_2H_6 are demonstrated in Fig. 1,*b*. The phonon-phonon component W_{pp} of the thermal resistance increases linearly with the temperature. The thermal resistance W_{pr} related to the translation-orientation interaction weakly grows with the temperature, and a slight acceleration of the growth rate is observed in the temperature range adjacent to the phase transition point. Such an increase of the W_{pr} growth rate can be associated with increase in the amplitude and the frequency of librations of C_2H_6 molecules with respect to the second-order axes [9]. The temperature dependences of the thermal resistance components for C_2H_6 are typical of orientationally ordered phases of molecular crystals [2]. At the same time, a small contribution of the translation-orientation component to the total thermal resistance is characteristic of orientationally disordered phases of molecular crystals, which are formed by highly symmetric molecules [2, 4].

4. Conclusions

The heat conductivity of solid C_2H_6 in the temperature range from 80 K to the melting temperature has been studied. As the temperature grows, the isobaric heat conductivity decreases and substantially exceeds the classical dependence $1/T$. The reduction of heat conductivity at the phase transition into the plastic bcc phase is 0.08 W/(m×K).The temperature dependence of

Reduced parameters and molar weights for Xe and C_2H_6

Substance	T_{cr}, K	Y_{cr}, cm^3/mol	μ	$W_{mol}(1/\Lambda_{mol})$, m·K/W
Xe	289.7	119.4	131.3	10.01
C_2H_6	305.3	148.0	30.0	8.77

the translation-orientation component W_{pr} of the total thermal resistance testifies (Fig. 1,*b*) that the rotational motion of methyl groups CH_3, in contrast to the rotational motion of whole molecules [2], does not affect the heat transfer in C_2H_6 substantially. This conclusion agrees well with the results of direct measurements of the isochoric heat conductivity of C_2H_6 [14], according to which it decreases with the temperature growth, similarly to what happens in orientationally ordered phases of molecular crystals [3].

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ІЗОБАРНА ТЕПЛОПРОВІДНІСТЬ КРИСТАЛІЧНОГО ЕТАНУ (C_2H_6)

О.І. Пурський

Р е з ю м е

Проведено дослідження ізобарної теплопровідності кристалічного C_2H_6 у діапазоні температур від 80 K і до початку плавлення. Теплопровідність зменшується при підвищенні температури. Зменшення в значеннях теплопровідності в результаті фазового $\beta \to \gamma$ переходу становить 0,08 Вт/м·К. Вплив орієнтаційного руху метильних груп CH_3 на теплопровідність досліджується за допомогою модифікованого методу зведених координат, шляхом виділення трансляційної і трансляційно-орієнтаційної компонент повного теплового опору.