Experimental evidence of the role of quasilocalized phonons in the thermal conductivity of simple alcohols in orientationally ordered crystalline phases

A.I. Krivchikov¹, F.J. Bermejo², I.V. Sharapova¹, O.A. Korolyuk¹, and O.O. Romantsova¹

¹B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine
47 Lenin Ave., Kharkov 61103, Ukraine
E-mail: krivchikov@ilt.kharkov.ua

²Instituto de Estructura de la Materia, CSIC, and Dept. Electricidad y Electrónica-Unidad Asociada CSIC, Facultad de Ciencia y Tecnología, Universidad del País Vasco/EHU, P.O. Box 644, E-48080-Bilbao, Spain

Received April 27, 2009

The thermal conductivity $\kappa(T)$ of crystalline alcohols (methyl, ethyl and 1-propyl) within their thermodynamic equilibrium phases for $T \geq 2$ K and under the equilibrium vapor pressures has been measured and analyzed. While such compounds usually exhibit a rich polymorphism including amorphous and partially ordered crystals, the phases here explored correspond to crystals showing complete orientational order. The results show that the temperature dependence of $\kappa(T)$ above its maximum deviates from the expected decrease following a $1/T$ law with increasing temperature arising from anharmonic interactions involving acoustic excitations. Such a deviation is here attributed to the presence of a component $\kappa_{II}(T)$ corresponding to the shortest-lifetime phonons (Cahill–Pohl model) additional to that $\kappa_{I}(T)$ related to propagating phonons and thus: $\kappa(T) = \kappa_{I}(T) + \kappa_{II}(T)$. Above $T = 40$ K $\kappa_{I}(T)$ does follow the law $1/T$ and $\kappa_{II}(T)$ is basically temperature independent. The component $\kappa_{I}(T)$ is well described by the Debye–Peierls model taking into account the phonon–phonon Umklapp processes and phonon scattering by dislocations. In turn, the contribution $\kappa_{II}(T)$ is attributed to the effects of higher lying excitations which get thermally populated above some 40 K. Finally, a systematic trend is found concerning the strength of phonon–phonon scattering which is seen to diminish as the number of carbon atoms in the alcohol molecule increases.

PACS: 66.70.–f Nonelectronic thermal conduction and heat-pulse propagation in solids; thermal waves; 63.20.–e Phonons in crystal lattices.

Keywords: heat transport, acoustic phonons, optical phonons, thermal conductivity, monoatomic alcohols.

Introduction

Alcohols are compounds containing one or several hydroxyl (OH) groups. According to the number of such groups, alcohols are subdivided into mono-, di-, three-hydric and so on. Primary monohydric alcohols result from substitution within the aliphatic molecular backbone of hydrogen or alkyl groups of different length by such an OH group. In common with other hydrogen-bonded (HB) systems such as normal water, the interactions between alcohol molecules are dominated by fairly strong directional forces identified with hydrogen-bonds which give rise to new properties of their condensed phases if compared to those exhibited by their parent aliphatic compounds. These result as a consequence of the co-operativity induced by the action of the HB’s which are of key importance to determine the structure of their condensed states. In fact, such HB’s make the molecules to form linear zigzag chains once the crystalline, thermodynamic ground state is attained. The crystal structure is then further stabilized by interchain Van der Waals forces. In other words, the stability of such compounds is governed by a balance between the relative strengths of HB, electrostatic and molecular dispersion interactions. Such a balance can be shifted by an increase in the aliphatic chain length since the relative strength of the latter kind of forces increases with the molecule...
length, or conversely, the strength of the co-operative HB interactions to determine the properties of these substances is known to decrease as the number of carbon atoms in the molecule backbone increases. Such a fact provides us with a handle to control the strength of HB interactions and thus to shed light on some still pending issues concerning the structure and dynamics of the most abundant HB system in the universe such is water in its dense-gas, liquid or solid forms.

Relatively rapid cooling of simple alcohols leads to supercooled liquid or glass phases, exception made of pure methanol which can only achieve a glassy state by means of special procedures such as vapor deposition on a cool substrate. Once within their solid states, simple alcohols exhibit a rich polymorphism. For example, ethanol (CH$_3$CH$_2$OH) can have three metastable long-lived phases under equilibrium vapor pressure — a structural glass, an orientationally disordered crystal with static disorder (orientational glass), a crystal with dynamic orientational disorder and an orientationally ordered crystal, which is the only stable thermodynamically equilibrium phase [1,2]. In turn, methanol (CH$_3$OH), which can be thought of as a water molecule where one of the hydrogens has been substituted by a methyl group, displays a more complex phase diagram with several crystal phases [3–6]. Under equilibrium vapor pressure methanol crystallizes into a high-temperature orientationally disordered β phase. On a further decrease in temperature a solid–solid transformation into a low-temperature orientationally ordered state (α phase) occurs at $T_{\alpha\beta} = 157.4$ K [6]. Polymorphism of the crystalline phases of methanol is determined by its H bonds, which are stronger than the dispersive molecular interactions, and by its simpler molecular structure in comparison to ethanol. The polymorphism of 1-propanol (CH$_3$CH$_2$CH$_2$OH, 1-Pr) is rather modest. Under equilibrium vapor pressure 1-propanol can change either into a glass or an orientationally ordered crystal.

Table 1 shows melting temperatures $T_m$, densities $\rho$, molar masses $M$ and space symmetry groups of methanol, ethanol and 1-propanol crystals.

The thermal conductivity $\kappa(T)$ of dielectric crystals composed by particles having orientational degrees of freedom within their orientationally ordered phases at temperatures above the phonon maximum usually decreases exponentially with rising temperature. On a further increase of temperature, most materials examined so far follow the $1/T$ law. It was found however that $\kappa(T)$ of some simple alcohols deviated from this law [1,2,10,11] but the reason for this behavior was not clear at that moment.

In this work we investigated phonon scattering in HB molecular crystalline alcohols where full orientational order has been achieved. In doing so, we can make use of well proven procedures for the analysis of thermal data since a true lattice exists and the amount of disorder present in our samples will only concern that derived from the intricacies of crystal growth. Furthermore, lattice dynamics models for methanol and ethanol are already available [12,13] which will allow us to assign specific features appearing in the analysis of the thermal conductivity to effects originated by proper crystal excitations. This contrasts with already reported results on the disordered phases, where the analysis of experimental data, has to be carried, by force, in terms of qualitative or semiquantitative procedures at best.

### Table 1. Parameters of methanol, ethanol and 1-propanol crystals

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_m$, K</th>
<th>$\rho$, kg/m$^3$</th>
<th>$M$, g/mol</th>
<th>Orientationally disordered crystal</th>
<th>Orientationally ordered crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>175.4</td>
<td>1015 [6]</td>
<td>32.04</td>
<td>Cmcm (β phase) [6]</td>
<td>$P2_1\overline{1}2_1$ (α phase) [6]</td>
</tr>
<tr>
<td>Ethanol</td>
<td>159</td>
<td>1070 [7]</td>
<td>46.07</td>
<td>bcc</td>
<td>$Pc$ monoclinic</td>
</tr>
</tbody>
</table>

The thermal conductivity was measured under equilibrium vapor pressure within the interval stretching from 2 K to $T_m$ using the method of steady-state linear heat flow [14]. The container for the sample [14] was a stainless steel tube. Two copper wires 1 mm in diameter were passed through the container perpendicular to its axis, which permitted measurement of the average temperature along the isothermal plane running across the sample. At the outer surface of the container copper sockets were soldered to the wires to cartridge two temperature sensors. The liquid alcohol sample was put in the container of the measuring cell under $^4$He gas flow. The helium gas was used to improve the heat exchange between the sample and the container. The container with the sample was vacuum-tight covered with the copper cap and an indium ring. A heater was fixed on the container cap to generate a downward heat flow in the sample.

A crystalline sample of methanol was prepared in the measuring container on slow cooling the liquid slightly below $T_m$. According to the chromatographic analysis,
the water content in pure methanol was less than 0.2% H₂O [11].

The ethanol sample was prepared in the state of a glass by very fast cooling of the liquid (over 50 K/min) passing through the temperature of glass formation $T_g$ to the boiling temperature of liquid nitrogen (the container with the sample at room temperature was immersed in liquid nitrogen). Above $T_g$ the sample melted into a supercooled liquid. On heating to 109 K the sample crystallized to an orientationally disordered metastable cubic phase and then transformed into an orientationally ordered state. The obtained crystal was annealed for 60 hours at the premelting temperature 156 K. The resulting orientationally ordered crystal had the lowest content of defects. Its maximum thermal conductivity was 1.9 times higher than that of the ethanol crystal in Refs. 1, 2. The purity of the ethanol was 99.8% and the water content was no more than 0.15%.

The 1-propanol sample was also prepared in the state of a glass. On heating it changed to a supercooled liquid and crystallized to an orientationally ordered crystal. It was annealed near $T_m$ for two days. The purity of 1-propanol was 99.9% (Chromasolv for high-performance liquid chromatography, SIGMA-ALDRICH Chemie Gmbh) [10].

The measurements were performed by gradually decreasing temperature. After reaching the lowest temperature point of the experiment the measurement was continued by a heating run increasing temperature. The measured values of the thermal conductivity were found to show no large hysteresis effects and thus were basically the same for cooling or heating runs.

The samples were prepared under the condition of multiple crystal nucleations which resulted finely grained polycrystals. They completely filled the measuring container and can thus be considered isotropic.

The temperature dependences of the thermal conductivities $\kappa(T)$ of methanol, ethanol and 1-propanol in their orientationally ordered crystal phases are shown in Fig. 1 in a double logarithmic plot. The $\kappa(T)$ curves display a bell-like shape typical of orientationally ordered crystals: from the high-temperature end, the thermal conductivity increases with decreasing temperature, then passes through a phonon maximum and finally it shows a decrease with decreasing temperature nearly following a quadratic temperature law. In the temperature region to the right of the phonon maximum, the increase of the thermal conductivity with decreasing temperature is the largest for ethanol and lowest for methanol. The latter has the highest $\kappa(T)$ at high temperatures and the lowest $\kappa(T)$ at low temperatures. The three alcohols have close thermal conductivities near 40–50 K.

At high temperatures the thermal conductivity of simple molecular crystals in the orientationally ordered phases is expected to follow the $1/T$ law [15–20]. As noticed above, here we observe a noticeable deviation of the curves $\kappa(T)$ from this law. This deviation becomes quite evident in data shown in Fig. 2 where the experimental results are plotted in terms of the product $\kappa(T) \cdot T$. For such plots, adherence to the law $1/T$ would lead for $T > 40$ K to a constant value for $\kappa(T) \cdot T$. Here we see from Fig. 2 that the product $\kappa(T) \cdot T$ follows a nearly linear law with a positive and finite slope. The finding is understood assuming that within this temperature region two mechanisms of phonon scattering contribute to heat transfer — the usual phonon–phonon scattering of heat and an additional mechanism independent of temperature. On such grounds, the temperature dependence of $\kappa(T)$ can be written as a sum

$$\kappa(T) = \frac{A}{T} + C,$$

where $A$ and $C$ are constants. The temperature dependence of $\kappa(T)$ can be written as a sum

$$\kappa(T) = \frac{A}{T} + C,$$
where the first term $\kappa/T$ describes the usual three-phonon Umklapp processes and the second term $C$ presents the additional mechanism of heat transfer that operates in the high-temperature region. The values for the fitting parameters $A$ and $C$ are given in Table 2.

Table 2. The fitting parameters for methanol, ethanol, 1-propanol

<table>
<thead>
<tr>
<th>Compound</th>
<th>$A$, W/m</th>
<th>$C$, W/(m·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>14.2</td>
<td>0.24±0.01</td>
</tr>
<tr>
<td>Ethanol</td>
<td>16.9</td>
<td>0.16±0.01</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>21.6</td>
<td>0.10±0.01</td>
</tr>
</tbody>
</table>

Since the second contribution $C$ is temperature independent, the high-temperature part of the curve $\kappa(T)$ can be described by the Cahill–Pohl model which assumes that a temperature-independent mechanism of thermal conductivity becomes dominant above the Debye temperature.

**Discussion**

The temperature dependence of the thermal conductivity of a crystalline solid is described quite accurately by the Debye–Peierls model for an isotropic solid. The model disregards the difference between the phonon modes of different polarizations:

$$\kappa(T) = \frac{k_B T}{2\pi^2 h^3 v} \int_0^\infty \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx,$$  \hspace{1cm} (2)

where $x = \hbar \omega/k_B T$, $\omega$ is the phonon frequency, $v$ is the speed of sound averaged over longitudinal and transverse polarizations, $\Theta$ is the Debye temperature and $\tau(x)$ is the effective relaxation time of the phonons participating in scattering. In general, $\tau$ includes a number of phonon scattering sources and in this particular case we write it as a sum of the relaxation time $\tau_1$ for phonons undergoing resistive scattering and that $\tau_\Pi$ for phonons having a mean-free-path comparable to the phonon half-wavelength (the so-called localized short-wavelength vibrational modes in the Cahill–Pohl model):

$$\tau = \tau_1 + \tau_\Pi.$$

In consequence, the integral describing the dependence $\kappa(T)$ in the orientationally ordered phases can be subdivided into two components:

$$\kappa(T) = \kappa_1(T) + \kappa_\Pi(T),$$

comprising that $\kappa_1(T)$ originated by propagating phonons able to transport heat whose mean free path is longer than the phonon half-wavelength and $\kappa_\Pi(T)$ which accounts for the additional mechanism of scattering according to the Cahill–Pohl model. The latter component, $\kappa_\Pi(T)$ refers to heat transfer processes mediated by localized harmonic short-wavelength vibrational modes, or by acoustic phonons with the mean free path equal to the phonon half-wavelength. The simplest description of $\kappa_\Pi(T)$ is provided by the phenomenological Cahill–Pohl model [21] that was proposed to interpret the thermal conductivity of amorphous solids at high temperatures. The simple model just sketched accounts adequately for the main features exhibited by the isochoric high-temperature thermal conductivity of molecular crystals within their orientationally ordered phases [22]. The model also makes use of the assumption that the shortest lifetime of each vibration is equal to the half-wavelength of the phonon wave $\tau = \pi/e$ [21]. The calculation was made using $\tau = F\pi/e$ where $F$ is the dimensionless fitting parameter allowing effectively for the intensity of the heat transfer by localized excitations, including the rotational ones. Then Eq. (2) becomes

$$\kappa_\Pi = F \frac{k_B^3 T^2}{2\pi h^3 v} \int_0^{\Theta/T} \frac{x^3 e^x}{(e^x - 1)^2} dx,$$  \hspace{1cm} (3)

$F = 1$ for the case when the phonon mean free path is equal exactly to the half-wavelength of the phonon wave; $F = 2$ in Ref. 23. For $T > \Theta \kappa_\Pi(T)$ becomes temperature independent. The Eqs. (2) and (3) were initially developed to build a model yielding the theoretical description of isochoric thermal conductivity and are widely used to analyse experimental data for crystalline and amorphous solids. Konstantinov et al. [22,24] were the first to include the contribution $\kappa_\Pi(T)$ within a model to represent the thermal conductivity of molecular crystals.

Here, we have adopted the approach just described to separate both components $\kappa_1(T)$ and $\kappa_\Pi(T)$ to the total thermal conductivity of simple primary alcohols. The results for methanol are taken as an example of the route followed to analyse our data and are shown in Fig. 3 in terms of $\kappa T$ plots as a function of temperature for the whole temperature interval together with data for the liquid taken from the literature [25]. Data for $T > 40$ K have been fitted using the approximation given by Eq. (1). In addition, $\kappa_\Pi(T)$ was calculated using Eq. (3) for the whole temperature interval so that at high temperatures $\kappa_\Pi(T)$ should coincide with the coefficient $C$ in Eq. (1). The experimental data also show that for temperatures about $T_m$, $\kappa_\Pi$ for the crystal comes close to the thermal conductivity for the liquid $\kappa_L$. In fact, there is no sign of a jump in the thermal conductivity at melting and the slopes followed by $\kappa_L$ and $\kappa_\Pi$ are quite similar. The component $\kappa_\Pi$ was calculated varying the parameter $F$ and using $\Theta$ and $\kappa$ from Table 3. The average sound velocity $\nu$ for methanol was calculated using the data for the longitudinal sound velocity [26]. $\Theta$ was obtained from the $\nu$ value. The contribution $\kappa_1$ is then estimated as a difference between the measured thermal conductivity $\kappa(T)$ and the component $\kappa_\Pi$. 

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Above 40 K $\kappa_1 \sim T^{-1}$, since as can be seen in Fig. 3 the product $\kappa_1T$ becomes independent of temperature. The contribution $\kappa_1$ to the thermal conductivity of methanol becomes dominant at lower temperatures.

The temperature dependences of the phonon-induced component $\kappa_1$ obtained from the thermal conductivity of the three alcohols are shown in Fig. 4 as a double-log plot. The behavior of $\kappa_1$ is similar in the three samples. Above 40 K $\kappa_1$ obeys the law $1/T$, which suggests that the contribution $\kappa_1$ is controlled by the $U$-processes in this region. At high temperatures $\kappa_1$ undergoes a slight variation: at $T = 100$ K it is 1.5 times higher in 1-propanol than in methanol. Besides, at high temperatures $\kappa_1$ displays a marked dependence molecular mass, that is, it grows as the mass increases. Below 40 K $\kappa_1$ of ethanol exceeds that of 1-propanol, thus pointing to the better quality of the ethanol sample because in this temperature region the phonon maximum is much determined by defects. At low temperatures ($T < 6$ K) $\kappa_1$ is proportional to $T^{-2}$ in all the three alcohols.

The component $\kappa_1$ obtained from experimental results was compared with the calculation based on the Debye–Peierls relaxation-time model using Eq. (2) allowing for the resistive $U$-processes of phonon scattering and also allowing for scattering by dislocations. The relaxation rate of phonons causing resistive scattering $\tau^{-1}_1$ is assumed to obey the Matthiesen rule and, therefore, can be written as a sum of rates representing different processes ($\tau^{-1}_i$),

$$\tau^{-1}_1(\omega, T) = \sum \tau^{-1}_i(\omega, T).$$

For an ordered crystal, the dominant mechanisms able to scatter heat-carrying phonons will concern anharmonic Umklapp processes with a rate $\tau^{-1}_U$, and scattering by dislocations $\tau^{-1}_{\text{dis}}$. Relevant expressions for all the scattering processes are given by:

$$\tau^{-1}_U(\omega, T) = B \omega^2 T \exp\left(-E_U/T\right),$$

$$\tau^{-1}_{\text{dis}}(\omega, T) = D_{\text{dis}} \omega,$$

where $B$ is the frequency factor, $E_U$ is the activation energy for the $U$-processes, and $D_{\text{dis}}$ is the dislocation scattering strength.

Table 3. Sound velocity $v$, Debye temperature $\Theta$, dimensionless fitting parameter $F$ allowing effectively for the intensity of the heat transfer by localized excitations, frequency factor $B$, activation energy $E_U$, and dislocation scattering strength $D_{\text{dis}}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v$, m/s</th>
<th>$\Theta$, K</th>
<th>$F$</th>
<th>$B$, $10^{-16}$s/K</th>
<th>$E_U$, K</th>
<th>$D_{\text{dis}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>1400 [26]</td>
<td>106</td>
<td>5±0.1</td>
<td>5.0</td>
<td>18</td>
<td>4.6·10^{-3}</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1600 [10]</td>
<td>112</td>
<td>3±0.1</td>
<td>4.4</td>
<td>27</td>
<td>1.1·10^{-3}</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>1888 [10]</td>
<td>121</td>
<td>2±0.1</td>
<td>2.9</td>
<td>19</td>
<td>3.1·10^{-3}</td>
</tr>
</tbody>
</table>

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The temperature dependences of $\kappa_1$ calculated for primary alcohols within the Debye–Peierls model allowing for the resistive $U$-processes of phonon scattering and the phonon scattering by dislocations are shown in Fig. 4 (color lines). The calculated curves describe the $\kappa_1$ contribution isolated from experimental data quite well. The parameters of resistive scattering calculated by Eqs. (4), (5) are shown in Table 3 alongside with the parameter $F$, the sound velocity $v$ and the Debye temperature $\Theta$.

The comparison of the experimental results and the calculation within the Cahill–Pohl model gives the parameter $F > 1$ (only the phonon states were taken into account). $F$ decreases as the molar mass increases. This result can be explained qualitatively as being caused by an additional contribution of the rotational and internal degrees of freedom of the molecule.

At high temperatures the thermal conductivity is strongly influenced by three-phonon processes which lead to a temperature dependence for this quantity following the $1/T$ dependence which results from a change in the thermal population of the phonon modes (e.g., see [15]). On the other hand, molecular crystals exhibit a substantial number of higher lying optical phonon branches, some of which show characteristic frequencies not too different from those of the optical branches at the Brillouin zone boundary. Considering as an example the well studied case of ethanol, we see there [12] that optical branches mostly involving molecular reorientations have characteristic frequencies as low as 1.2 THz, which means that they will be largely populated for temperatures above 40 K and thus contribute with a source of additional scattering.

Current theoretical approaches for phonon–phonon scattering processes are able to formulate at best, semiquantitative predictions concerning the temperature dependence of the thermal conductivity [15,20]. The theory of phonon–phonon scattering is however able to provide an estimate for the coefficient $A$ of the $T^{-1}$ term in Eq. (1). In fact, such a coefficient can be calculated for molecular crystals by Slack’s approximation [27], as [20]:

$$ A = 2 \left( \frac{\kappa_B^2}{\Theta} \right) \frac{T_m}{h} \left( \frac{\rho N_A}{6\pi^2 M} \right)^{1/3}, \quad (6) $$

where $N_A$ is the Avogadro number and $M$ is the molecular mass. Besides, the coefficient $A$ can be calculated by Slack’s equation [23] for cubic atomic crystals with over two atoms per unit cell

$$ A = \frac{3 \cdot 10^7 M^{3/2}}{\gamma^2 n^{2/3}} \left( \frac{M}{\rho N_A} \right)^{1/3}, \quad (7) $$

were $\gamma$ is the Grüneisen constant, $n$ is the number of atoms per unit cell: $\gamma = 2.5$ for the investigated crystals, $n = 4$ for methanol and ethanol [6,9] and $n = 6$ for 1-propanol [28]. The dependence of the coefficient $A$ on the molar mass calculated by Eqs. (6), (7) for simple methyl, ethyl and 1-propyl alcohols is shown in Fig. 5 alongside with experimental results. The theoretical estimate by Eq. (6) is there shown to depart from experiment both in the absolute values as well as in the trend with increasing temperature. The observations did not come as a surprise and provide a vivid reminder of the action of excitations other than those identifiable as translational lattice vibrations. In fact, at high temperatures one expect higher lying modes within the dispersion relations of these crystals to become thermally populated and thus, account needs to be made to incorporate the effects of molecular librations as well as other rotational motions either involving whole molecules or segments of them. The experimental results show that the coefficient $A$ increases concomitantly with the molecular mass, whereas the calculation predicts the opposite. The largest discrepancy between experiment and calculation is found for methanol which shows a theoretical estimate three times larger than the measured value whereas such a discrepancy is reduced as the mass of the molecule increases. The theoretical estimation by Eq. (7) accounts only for the phonon–phonon scattering in an atomic cubic crystal and disregards other scattering mechanisms. It does not therefore describe experimental data.

In our quest to understand the results here reported on the ordered crystal phases we have examined some recent literature data concerning nonlinear effects in molten alcohols. In fact, although it is not usually stated in explicit form, propagation of heat-carrying excitations through condensed media is fundamentally nonlinear in nature. The strength of such nonlinear behavior is simply related to the ratio of the third to second virial coefficients ($B/A$) of the equation of state of the material. Recent advances

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**Fig. 5.** The coefficient $A$ versus molar mass at $T = T_m$: ○ — experiment, ▲ — theory of phonon–phonon scattering for molecular crystals [20] (see Eq. (6)), ■ — theory of phonon–phonon scattering for atomic crystals [23] (see Eq. (7)). Lines are smoothed data.
by ultrasonic and optical spectroscopy techniques [29–32] enable the measurement of this ratio directly either by determination of the rate of change in sound speed with pressure or by measurement of optical saturation absorption coefficients as well as nonlinear refraction. Within the liquid state, such nonlinear coefficient can be related to molecular properties such as internal pressure, cohesive energy or the diffusion coefficient or the rotational correlation time. Although there is considerable scatter in the literature values for \( B/A \), the general trend concerning its dependence with molecular structure remains the same in all reported studies. In fact the measured values of the ratio \( B/A \) show a systematic trend with the alcohol chain length and go from a value of about 8.6 for methanol to 9.54 for 1-propanol and 9.73 for 1-butanol. Particular attention merits the estimation of an elusive quantity such is the internal pressure on the basis of ultrasonic measurements for the liquids [29]. Such a quantity measures the strengths of forces making the molecules of a medium to be bound together and thus includes the forces that arise due to pure van der Waals’ interactions, the attractive forces generated from HB interactions as well as the pressure due to the thermal molecular motion. The derived values go from about 110 MPa for methanol down to about 86 MPa for propanol. In turn, estimates for the cohesive energies go from 28.7 kJ/mol for methanol to 45.86 kJ/mol for propanol.

The picture that thus emerges from studies within the liquids provides us with a tool to understand our observation of the increasing strength of nonlinear interactions within the crystals as measured by the \( A \) coefficient in Eq. (1) with increasing molecular mass which are enhanced some 11 per cent in going from crystalline methanol to propanol. The result which may seem counterintuitive and also goes against prediction from simple treatments such as that given by Eq. (6). Indeed, does however fit perfectly with results concerning the liquids just referred to where the increase in strength of the nonlinear effects in going from methanol up to propanol amounts some fifty per cent.

**Conclusion**

The present work shows from comparison and analysis of experimental data for some simple crystalline alcohols with a complete orientational order at \( T > 2 \) K under their equilibrium vapor pressure that the thermal conductivity \( \kappa(T) \) of these objects deviates from the law \( 1/T \). The deviation is attributed to the component \( \kappa_{\|}(T) \) corresponding to the shortest-lifetime phonons (Cahill–Pohl model) which appears in the thermal conductivity in addition to the component \( \kappa_{\bot}(T) \) accounting for the propagating phonons: \( \kappa(T) = \kappa_{\|}(T) + \kappa_{\bot}(T) \). The microscopic origin of such an additional contribution is unambiguously identified with higher lying molecular excitations involving internal motions which, as shown in detail in a case example for ethanol [12], do have complex mode eigenvectors. Once the contribution of this additional source is taken care of, an experimental separation of that \( \kappa_{\|}(T) \) due to propagating acoustic phonons is achieved. The latter behaves as expected for a molecular crystal, showing above \( T \approx 40 \) K \( \kappa_{\|}(T) \) a decrease with increasing temperature in accordance with the \( 1/T \) law. Furthermore, \( \kappa_{\|}(T) \) is shown to be well described by the Debye–Peierls model, which allows for the phonon–phonon Umklapp processes and the phonon scattering by dislocations.

Analysis of the temperature dependence of the coefficient measuring the strength of the phonon–phonon scattering processes shows that it increases as the number of carbon atoms in the alcohol molecule increases. The result is easily understood in terms just explained, since the larger the molecular backbone, the denser will be the mesh of optical excitations lying above the acoustic branches.

Finally, the results here reported on warn about some oversimplified routes for the analysis of experimental data on these materials (see [1] and references therein) where it is assumed that all relevant excitations at temperatures close to melting concern purely propagating acoustic modes.

**Acknowledgment**

The authors are sincerely grateful to Yu.A. Dmitriev, V.A. Konstantinov, and Prof. V.G. Manzhelii for helpful discussions and interest in this study. The investigations is made on the competition terms for joint projects of NAS of Ukraine and Russian Foundation for Fundamental Research (Agreement N 9-2008, Subject: «Collective processes in metastable molecular solids»).


