

Thermal conductivity of molecular crystals of monoatomic alcohols: from methanol to butanol

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Experimental data on the thermal conductivity $\kappa(T)$ of some simple alcohols have been compared, analyzed and generalized. The objects of investigation were methyl, protonated and deuterated ethyl, 1-propyl and 1-butyl alcohols in the thermodynamically equilibrium phase with a complete orientational order. The temperature interval was from 2 K to the melting point under the equilibrium vapor pressure. It is found that in the region above the temperature of the maximum thermal conductivity $\kappa(T)$ deviates from the $1/T$ law. This is because the total thermal conductivity has an extra contribution $\kappa_{II}(T)$ of short-lived phonons in addition to $\kappa_I(T)$ contributed by propagating phonons: $\kappa(T) = \kappa_I(T) + \kappa_{II}(T)$. The contribution $\kappa_I(T)$ is well described by the Debye–Peierls model allowing for the phonon–phonon processes and scattering of phonons by dislocations. At $T > 40$ K the contribution $\kappa_I(T)$ obeys the law A/T and $\kappa_{II}(T)$ is practically temperature-independent. It is shown that the Debye temperature Θ_D of alcohol is dependent on the molecular mass as $\Theta_D = 678M^{-0.42}$ K and the coefficient A characterizing the intensity of the phonon–phonon scattering increases with the molecular mass of the simple monoatomic alcohol by the law $A = 0.85M^{0.8}$ W/m, which suggests a decreasing intensity of the phonon–phonon process.

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Introduction

The temperature dependence of the thermal conductivity of simple dielectrically-perfect crystals with orientational degrees of freedom usually has the shape of bell. The thermal conductivity in the low-temperature region of the curve is determined by the grain-boundary scattering of phonons and obeys the law T^3 [1]. As the temperature rises, a maximum of thermal conductivity appears in the curve, its height being dependent on the crystal quality. On further heating, the thermal conductivity decreases exponentially and finally changes to the law $1/T$ (e.g., see [2–7]). This law is determined by the processes of phonon–phonon scattering.

In addition to acoustic phonon modes, molecular crystals with several molecules per unit cell also have localized short-wavelength vibrational modes which can cross the acoustic branches. This influences the temperature behavior of the thermal conductivity in the region above the temperature of the phonon maximum. It has been shown recently that localized short-wavelength vibrational modes are considerably important for the thermal conductivity of

simple molecular orientationally-ordered hydrogen-bonded crystals under the equilibrium pressure [8]. The thermal conductivity investigated [8] in three simple monoatomic alcohols in the orientationally-ordered phase exhibited a deviation from the law A/T in the high-temperature region (A is a coefficient characterizing the intensity of phonon–phonon scattering, which is dependent on the number of C atoms in the alcohol molecule). The law A/T cannot describe the behavior of the isochoric thermal conductivity of cryocrystals [9].

Primary monoatomic alcohols are organic compounds consisting of a carbon skeleton with a hydroxyl group OH at its end. The alcohol molecule is “flexible” as to the bond length between the carbon skeleton and the hydroxyl group and the angle between the carbon skeleton and the OH group. Such flexibility is an additional source of low-energy intramolecular local vibrations in the alcohol crystal [10]. Simple monoatomic alcohols are very interesting objects to investigate, especially ethyl alcohol which exhibits rich polymorphism in the condensed phase [10–12].

On cooling primary alcohols are readily supercooled and form glasses. The thermal conductivity in such glasses demonstrate rather unusual behavior. For example, at low temperatures it is dependent on the number of C atoms in the alcohol molecule [13]. On crystallization into the orientationally-ordered phase, the molecules of a monoatomic alcohol form a chain-like structure due to the H bonds.

This study presents a detailed analysis of the thermal conductivity of molecular crystals of monoatomic orientationally-ordered alcohols in the series from methanol to 1-butanol including deuterated ethanol. The general regularities of the temperature dependence of the thermal conductivity have been revealed for molecular crystals of orientationally-ordered alcohols. It is shown that the coefficient A characterizing the intensity of phonon–phonon scattering increases almost linearly with the molecular mass of the simple monoatomic alcohol.

Experiment and discussion

The thermal conductivity of crystalline alcohols was measured under the equilibrium vapor pressure in the setup developed by [14] using the flat steady — state potentiometric method at temperatures from 2 K to the melting point T_m . The sample preparation is detailed elsewhere [8,15,16]. The deuterated C_2D_5OD alcohol (D purity was 99%, anhydrous) was supplied by Cambridge Isotope Laboratories, Inc. The concentration of hydrogen isotopic defects was 1%. The crystals of protonated and deuterated ethyl, 1-propyl and 1-butyl alcohols in completely orientationally-ordered thermodynamically-equilibrium phase were obtained from the glass state by gradual heating through several successive metastable states. Each sample was long-annealed near T_m . The thermal conductivity was investigated for two methanol samples [15], one high quality sample of hydrogenated ethanol [8] and some middle quality samples of hydrogenated ethanol [17], one sample of 1-propanol [18], one sample of 1-butanol [16], and four samples of deuterated ethanol [19].

The measured temperature dependences of the orientationally-ordered crystals of methanol [15], deuterated ethanol [19] and 1-butanol [16] are illustrated in the double logarithmic coordinates in Fig. 1. The curves have the bell-like shape typical of orientationally-ordered crystals. They have a distinct phonon-induced maximum of $\kappa(T)$ at $T = 14.2$ K in deuterated ethanol, $T = 17.1$ K in methanol and $T = 28$ K in 1-butanol. Deuterated ethanol and 1-butanol have close maximal thermal conductivities. The maximal thermal conductivity of methanol is somewhat lower, which indicates a worse quality of the crystal. Below T_{\max}^{ph} the thermal conductivity of the alcohols is close to the quadratic temperature dependence which corresponds to the processes of phonon scattering at dislocations. Above T_{\max}^{ph} the thermal conductivity of the alcohols decreases with the temperature rise. This corresponds to the effective

processes of phonon–phonon scattering [8,15]. In 1-butyl alcohol the thermal conductivity is the lowest at low temperatures and the highest at high temperatures. Above $T = 40$ K the thermal conductivity deviates obviously from the expected dependence $1/T$. It is seen that in this temperature region the heat transport is effected not only through the phonon–phonon mechanism of heat dissipation following the dependence $1/T$ but is contributed by an additional mechanism independent of temperature. On this basis the temperature dependence of the thermal conductivity $\kappa(T)$ can be presented as a sum [8]

$$\kappa(T) = A/T + C. \quad (1)$$

The first term A/T characterizes the resistive processes of phonon–phonon scattering. The term C refers to the additional mechanism of heat transport by localized short-wavelength vibrational modes, or phonons whose mean free path is comparable with the phonon half-wavelength. The dependence $A/T + C$ for the crystal 1-butanol at $T > 40$ K (black thick line) along with the dependence A/T (red line) for coefficients $A = 28.0$ W/m and $C = 0.32$ W/(m·K) are illustrated in Fig. 1.

Table 1 carries the coefficients A and C of Eq. (1) for some simple alcohols along with their molar masses, spatial symmetry groups, melting temperatures T_m , Debye temperatures Θ_D and the coefficients C_D at T^3 derived from heat capacity data. Θ_D of some crystals of simple monoatomic alcohols were calculated using the coefficient C_D at T^3 obtained by the Spanish researchers investigating the heat capacity of alcohols [12,20]. Coefficients A for 1-butanol and methanol were obtained with accuracy 3–4% and for deuterated ethanol accuracy of coefficient A is 9%.

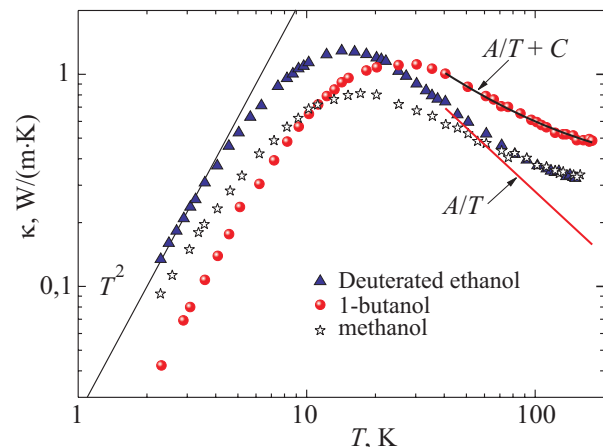


Fig. 1. The temperature dependences of the thermal conductivity of methyl [15], deuterated ethyl [19], and 1-butyl [16] alcohols in the orientationally-ordered phase. The dependence $A/T + C$ for the crystal 1-butanol at $T > 40$ K (black thick line) along with the dependence A/T (red line) for coefficients $A = 28.0$ W/m and $C = 0.32$ W/(m·K) are illustrated in this picture.

Table 1. The molar mass M , melting temperature T_m , Debye temperature Θ_D , coefficient C_D at T^3 obtained from heat capacity data for alcohols [12,20], spatial symmetry groups of orientationally-ordered crystals and the coefficients A and C for 1-butanol (this study), deuterated ethanol [19], methanol, protonated ethanol and 1-propanol [8]

Alcohol	M , g/mol	A , W/m	C , W/(m·K)	Space groups	T_m , K	C_D , mJ/(mol·K ⁴)	Θ_D , K
Methanol	32.04	14.2	0.24±0.01	$P2_12_12_1$ orthorhombic [21]	175.37 [21]		158 * 106 [15]
Ethanol-H	46.07	16.9	0.16±0.01	Pc monoclinic [24]	159 [11]	0.766 [12]	136
Ethanol-D	52.11	20.1	0.18±0.01	Pc monoclinic [25]	159 [12]	0.906 [12]	129
1-Propanol	60.09	21.6	0.10±0.01	$P2_1/m$ monoclinic [22]	148 [12]	1.10 [12]	121
1-Butanol	74.12	28.0	0.32±0.01	triclinic [23]	183.5 [23]	1.40 [20]	112 [20]

* — extrapolation

As the mass of the alcohol molecule increases, the coefficient C has nonmonotonic dependence, the coefficient A increases, which points to a reduction of the phonon-phonon scattering intensity.

The second temperature-independent contribution in Eq. (1) can be described by the phenomenological Cahill–Pohl model [26], which assumes that in the approximation of the Debye phonon spectrum of the isotropic medium (the difference in the polarizations of the phonon modes is disregarded) the shortest lifetime of each vibration is equal to its half-period $\tau = \pi/\omega$ [26].

Traditionally, the temperature dependence of thermal conductivity is described quite accurately by the Debye–Peierls model of an isotropic solid. Using this model the expression $\kappa(T) = \kappa_I(T) + \kappa_{II}(T)$ can be obtained conceiving the effective $\kappa(T)$ as a sum of the contribution $\kappa_I(T)$ of the phonons inducing resistive scattering and $\kappa_{II}(T)$ of the phonons whose mean free path is equal to the phonon half-wavelength (the so-called localized short-wavelength vibrational modes in the Cahill–Pohl model).

The thermal conductivity of the methanol–1-butanol series of alcohols in the orientationally-ordered phase was thus separated into two constituents $\kappa_I(T)$ and $\kappa_{II}(T)$. The component κ_{II} was calculated within the Cahill–Pohl model by Eq. (3) of Ref. 8 for the whole temperature interval. The contribution κ_{II} is rather insignificant at low temperatures but it increases with a rising temperatures and becomes determining at high temperatures. It accounts for the high-energy excitations that are thermally activated above 40 K. $\kappa_{II}(T)$ of deuterated ethanol and 1-butanol was calculated using the Θ_D data of Table 1 and sound velocities v obtained from the Θ_D data allowing for the density ρ : $\rho = 1213 \text{ kg/m}^3$ [25], $v = 1795 \text{ m/s}$ in deuterated ethanol and $\rho = 1318.5 \text{ kg/m}^3$ [23], $v = 1704 \text{ m/s}$ in 1-butanol.

The dependence of the Debye temperature Θ_D of some monoatomic alcohols on the molecular mass is shown in Fig. 2 in the double logarithmic coordinates. Unfortunately, there are no direct data on the Debye temperature of methanol. $\Theta_D = 106 \text{ K}$ was estimated [15] from the longitudinal sound velocity [27]. Nevertheless, the Θ_D values obtained for other alcohols fall quite accurately on the dependence $\Theta_D = 678M^{-0.42} \text{ K}$, which makes it possible to

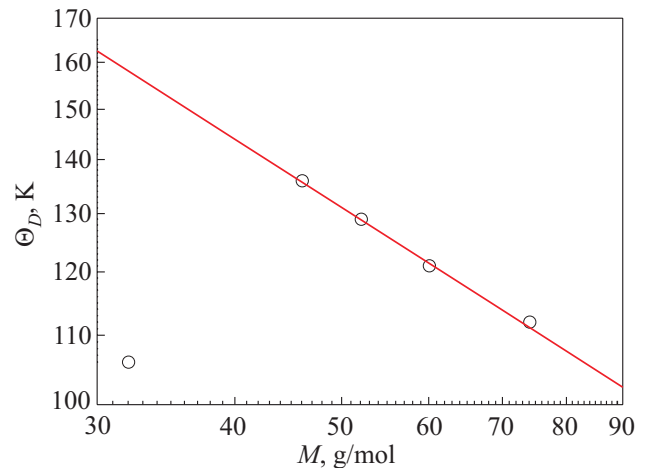


Fig. 2. The Debye temperature Θ_D of simple monoatomic alcohols as a function of the mass of the alcohol molecule. The line illustrates the dependence $\Theta_D = 678M^{-0.42} \text{ K}$.

extrapolate $\Theta_D = 158 \text{ K}$ for methanol. The dependence of Θ_D on the mass of the molecule agrees with the dependence $\Theta_D \sim M^{-1/2}$ in [10]. The decrease in Θ_D with the increasing molecular mass indicates that the frequency interval of the acoustic modes reduces. In the investigated series of alcohols the region of acoustic frequencies was the largest in the methanol crystal and the smallest in 1-butanol. This refers to the effective spectrum of vibrational states in the Debye model. As the number of C atoms in the alcohol molecule increases, the crossing of the local and acoustic modes occurring in alcohols with a small number of C atoms in the molecule [10] shifts gradually beyond the acoustic frequency region because the acoustic region reduces. This is one of the factors suppressing the intensity of phonon–phonon scattering when the mass of the alcohol molecule increases.

The phonon contribution κ_I was obtained as a difference between the measured total thermal conductivity $\kappa(T)$ and the component κ_{II} . At high temperatures $\kappa_I(T)$ obeys the law $1/T$. The component κ_I was then compared with the value calculated within the Debye–Peierls relaxation model using Eq. (2) of Ref. 8 allowing for the resistive U-pro-

cesses of phonon scattering and also allowing for scattering by dislocations. The relaxation rate of phonons causing resistive scattering τ_1^{-1} is assumed to obey the Matthiessen rule and, therefore, can be written as a sum of rates representing different processes τ_i^{-1} :

$$\tau_1^{-1}(\omega, T) = \sum_i \tau_i^{-1}(\omega, T).$$

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

$$\tau_U^{-1}(\omega, T) = B \omega^2 T \exp(-E_U/T), \quad \tau_{\text{dis}}^{-1}(\omega, T) = D_{\text{dis}} \omega,$$

where B is the frequency factor, E_U is the activation energy for the U-processes, and D_{dis} is the dislocation scattering strength. It is found that the Debye–Peierls model describes the phonon component $\kappa_I(T)$ of the investigated alcohols quite accurately.

At high temperatures the intensity of the phonon–phonon processes in crystals is characterized by the coefficient A of Eq. (1) which can be estimated proceeding from the theory of phonon–phonon scattering. Knowing the melting temperature the coefficient A of molecular crystals can be calculated by Slack’s [28] formula as [7]

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

where N_A is the Avogadro constant. The coefficient A for cubic atomic crystals with $n > 2$ atoms per unit cell can be calculated by Slack’s equation [29]:

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

where γ is the Grüneisen constant equal to $\gamma = 2.5$ for the investigated crystals with $n = 4$ for methanol, ethanol and 1-butanol [21–23], and $n = 6$ for 1-propanol [24]. The dependence of the coefficient A upon the mass of a simple monoatomic alcohol molecule is illustrated in Fig. 3 in the double logarithmic coordinates (experimental results and calculation by Eqs. (2), (3)). It is seen that the coefficient A increases almost linearly with the molar mass of simple alcohols and falls quite well on the dependence $A = 0.85M^{0.8}$ W/m. The theory of phonon–phonon processes does not describe the behavior of the coefficient A particularly in the case of low molar masses. The discrepancy between theory and experiment reduces as the molar mass increases. Equation (2) describes the experimental results more accurately than Eq. (3). The growth of the coefficient with the mass of the alcohol molecule implies that at high temperatures the thermal conductivity increases with the mass of the alcohol molecule. Hence, the intensity of pho-

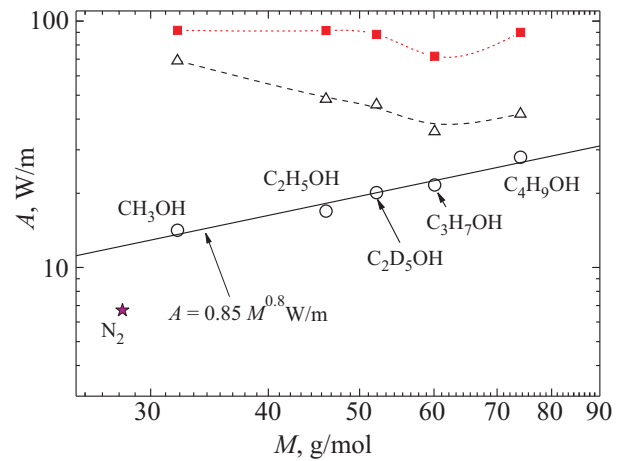


Fig. 3. The coefficient A as a function of the molar mass of simple alcohols: experiment (○), literature data for N_2 (★) [4]. Theory of phonon–phonon scattering: molecular crystals [7] (see Eq. (2)) (Δ); atomic crystals [29] (see Eq. (3)) (■); solid line — dependence $A = 0.85M^{0.8}$ W/m.

non–phonon scattering decreases. For comparison, Fig. 3 carries the coefficient A obtained from the thermal conductivity data for nitrogen [4] in the orientationally-ordered phase. This value cannot be described by the above A -vs-mass dependence.

Conclusions

The data on the thermal conductivity of a series of simple monoatomic alcohols from methanol to 1-butanol in the crystalline phase with a complete orientational order under equilibrium pressure have been analyzed. It is found that above the temperature of the maximum thermal conductivity $\kappa(T)$ deviates from the expected law $1/T$, which follows from anharmonic interactions of acoustic excitations. The deviation is due to the contribution $\kappa_{II}(T)$ of short-lived phonons, which appear in the total thermal conductivity in addition to the contribution $\kappa_I(T)$ of propagating phonons: $\kappa(T) = \kappa_I(T) + \kappa_{II}(T)$. The additional $\kappa_{II}(T)$ is due to localized short-wavelength vibrational modes in the Cahill–Pohl model. It is shown that the Debye temperature Θ_D is dependent on the mass of the alcohol molecule as $\Theta_D = 678M^{-0.42}$ K and the coefficient A characterizing the intensity of phonon–phonon scattering increases with the molar mass of the simple monoatomic alcohol following the law $A = 0.85M^{0.8}$ W/m, which corresponds to a decrease in the intensity of the phonon–phonon scattering. This behavior is due to the fact that in alcohol crystals with an orientational order acoustic phonons modes are hybridized with localized short-wavelength vibrational modes.

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