

# ISOBARIC HEAT CONDUCTIVITY OF ORIENTATIONALLY ORDERED MOLECULAR CRYSTALS

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By the example of solid  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CO}_2$ , we analyze the high-temperature isobaric heat conductivity of orientationally ordered molecular crystals. The isobaric heat conductivity is described in the frame of the Debye approximation with regard for the effects of heat expansion and the limitation on the free path length of phonons. It is established that the temperature dependence of the isobaric heat conductivity of orientationally ordered molecular crystals is determined, at  $T \geq \Theta_D$ , by  $U$ -processes, the heat expansion of specimens under study, and the approach to the minimum value of heat conductivity.

ourselves by the account of translational oscillations of molecules at sites of the crystal lattice and the orientational motion of molecules as a whole.

In the present work, by the example of solid  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CO}_2$ , we carry out the numerical analysis of the isobaric heat conductivity of orientationally ordered crystals. The analysis is performed in the frame of the Debye approximation with regard for the effect of heat expansion and the effect of the minimum of heat conductivity.

## 1. Introduction

Simple molecular crystals possess a number of peculiarities which influence significantly the dynamics of a crystal lattice. In molecular crystals, along with translational oscillations of molecules, it is necessary to consider the orientational movement of molecules as a whole, intramolecular rotation of segments of molecules, and intramolecular oscillations. Specific features of the dynamics of the translational and orientational subsystems of crystals affect their thermodynamic properties and must manifest themselves in one way or another in the processes of relaxation. This is related, first of all, to the translational-orientational interaction that is characteristically reflected on the kinetic properties of molecular crystals, in particular, on the heat conductivity [1, 2]. The account of each additional kind (as compared with that in atomic crystals) of heat motion hampers significantly the construction of theoretical models. The energy of intramolecular coupling in simple molecular crystals exceeds considerably the energy of intermolecular interaction. Respectively, intramolecular oscillations give no remarkable contribution, as a rule, to the dynamics of a crystal even in the region of premelting temperatures [3]. Thus, while considering the heat motion in simple molecular crystals, we may restrict

## 2. Results and Their Discussion

The estimates executed by different researchers in the frame of the three-phonon theory gave the following expression for the high-temperature behavior of the heat conductivity of dielectric crystals [4]:

$$\Lambda = K \frac{ma\Theta_D^3}{\gamma^2 T}, \quad (1)$$

where  $m$  is the mean atomic (molecular) mass,  $a$  is the lattice constant,  $\gamma = -(\partial \ln \Theta_D / \partial \ln V)_T$  is the Grüneisen parameter,  $\Theta_D$  is the Debye temperature, and  $K$  is the numerical coefficient.

From the viewpoint of conditions of the execution of experiments, the temperature dependences of heat conductivity are studied on isobars and isochors. For the law  $1/T$  to be satisfied, it is necessary that the crystal volume be invariable. Otherwise, the modes will vary, which will lead to the other temperature dependence of heat conductivity. In the region of low temperatures ( $T \leq \Theta_D/4$ ), the values of the coefficients of heat expansion are insignificant. But, with increase in temperature in the region of high temperatures ( $T \geq \Theta_D$ ), the heat expansion induces essential changes in the volume which cause the deviation from the above-mentioned law. The results of most experiments [1,4] show that the high-temperature heat conductivity of

molecular crystals at a constant pressure depends on temperature as  $\Lambda \propto T^{-k}$ , where  $1 < k < 2$ . The effect of heat expansion on heat conductivity can be estimated by comparing the isobaric and isochoric heat conductivities at the same temperature. As a rule, the majority of experiments is carried out under isobaric conditions. Therefore, the direct comparison of experimental data with theoretical ones can be performed not in all the cases. With a high degree of reliability, the isochoric heat conductivity can be determined by the recalculation of isobaric data to a constant density by the formula [1]

$$\Lambda_v = \Lambda_p \left( \frac{V(T)}{V_0} \right)^g, \quad (2)$$

where  $\Lambda_v$  and  $\Lambda_p$  are the isochoric and isobaric heat conductivities,  $V(T)$  is the molar volume of a free specimen as a function of temperature,  $V_0$  is the molar volume, to which the recalculation is carried on, and  $g$  is the Bridgman coefficient ( $g = (\partial \ln \Lambda / \partial \ln V)_T$ ) (Table). In Fig. 1, we present the values of  $\Lambda_v$  calculated by formula (2). The recalculation was performed to constant molar volumes  $V_{\text{mol}}^{\text{CHCl}_3} = 59.5 \text{ cm}^3/\text{mole}$ ,  $V_{\text{mol}}^{\text{CH}_2\text{Cl}_2} = 47.1 \text{ cm}^3/\text{mole}$ ,  $V_{\text{mol}}^{\text{CO}_2} = 26.2 \text{ cm}^3/\text{mole}$  occupied by the specimens under study at a temperature of 80 K. The obtained values agree well with the results of direct measurements of isochoric heat conductivity [5,6] under identical conditions ( $P, V, T$ ). The isobaric heat conductivity of the crystals under study reveals the temperature dependences  $\Lambda_p^{\text{CHCl}_3} \sim T^{-1.19}$  [7],  $\Lambda_p^{\text{CH}_2\text{Cl}_2} \sim T^{-1.21}$  [8],  $\Lambda_p^{\text{CO}_2} \sim T^{-1.09}$  [3], whereas the isochoric heat conductivity of these crystals depends on temperature as  $\Lambda_v^{\text{CHCl}_3} \sim T^{-0.88}$ ,  $\Lambda_v^{\text{CH}_2\text{Cl}_2} \sim T^{-0.85}$ ,  $\Lambda_v^{\text{CO}_2} \sim T^{-0.68}$  (Fig. 1). It is seen from the presented dependences that a change of the volume of a specimen under study with variation in temperature is one of the main reasons for significant deviations of the isobaric heat conductivity from the theoretically predicted dependence  $1/T$ . At the same time, the orientational motions of molecules in molecular crystals affect significantly [1, 2, 5] both the absolute value of heat conductivity and the character of its temperature dependence.

The main complexity of a description of the orientational subsystem consists in the significant

#### Parameters of the Debye model of heat conductivity and the Bridgman coefficients

Substance	$\alpha$	$A, 10^{-16} \text{ s/K}$	$\gamma$	$g$
CHCl <sub>3</sub>	1.81	1.46	3.1	3.9
CH <sub>2</sub> Cl <sub>2</sub>	1.3	1.50	2.9	4.6
CO <sub>2</sub>	1.6	1.01	2.5	5.7

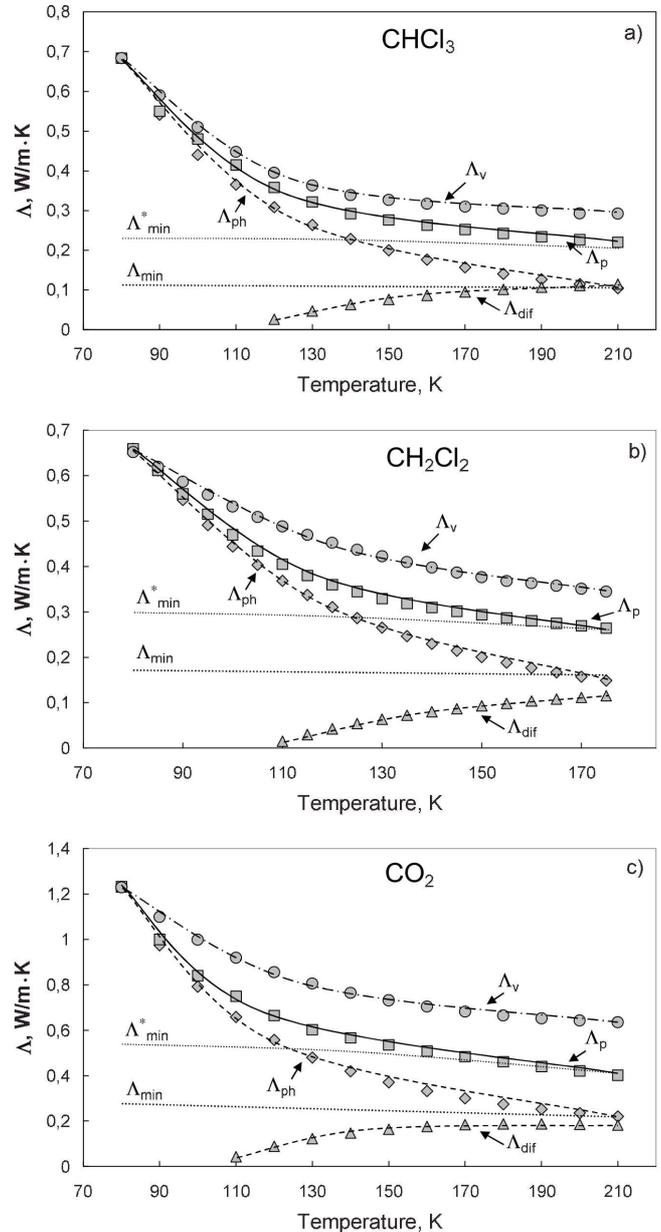


Fig. 1. Heat conductivities of solid CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and CO<sub>2</sub>. Squares – experimental isobaric data [3, 7, 8], the solid line – values of  $\Lambda_p$  calculated by relation (7);  $\Lambda_{\text{ph}}$  and  $\Lambda_{\text{dif}}$  – the contributions of phonons and “diffusive” modes to the heat transfer, respectively;  $\Lambda_v$  – the isochoric heat conductivity obtained by the recalculation by relation (2); and  $\Lambda_{\text{min}}$  and  $\Lambda_{\text{min}}^*$  – minima of the isobaric heat conductivity calculated by relations (5) and (10), respectively

anharmonicity of libratory motions. It follows from the estimation of the amplitudes of librations and the analysis of thermodynamic properties of molecular

crystals that anharmonic effects in the orientational subsystem are essential even at temperatures much less than the temperature of orientational ordering of these crystals, whereas translational oscillations can be described with a high degree of reliability in the harmonic approximation [9]. In molecular crystals, the orientational motion of molecules can vary from small-amplitude low-frequency librations to the practically free rotation, depending on a specific substance and temperature. It is quite logical that these processes must influence the behavior of thermal properties. On the gradual transition of molecules to the free rotation, the contribution of this type of heat motion to heat capacity tends asymptotically to the heat capacity of a system of free rotators, and the relevant contributions to heat expansion and heat conductivity tend to zero [3]. The last assertion requires at least a simple explanation. An increase in the angular amplitude of librations cannot occur without increase in the effective volume of a molecule. As a result, this leads to an additional contribution to the heat expansion of a crystal. Free rotation of molecules means the absence of the interaction with translational oscillations and rotations of other molecules. On the free rotation, there is no additional scattering of phonons, which leads to the absence of the effect of rotational motion of molecules on heat conductivity. From this viewpoint, the situation concerning the behavior of the high-temperature heat conductivity of solid  $\text{CH}_4$  looks to be rather demonstrative [10]. In simple molecular crystals, the scattering of phonons by orientational excitations of a crystal lattice can be of the order of the phonon-phonon one. Moreover, in the case where, with increase in temperature, the diminution of the phonon-libron heat resistance exceeds the increase in the resistance due to the phonon-phonon scattering caused by the gradual transition of molecules to a retarded rotation, the heat conductivity of a crystal can grow [11,12]. The transition to a retarded rotation can occur in crystals formed from highly symmetric molecules with a low-energy barrier hampering the rotation. As for the crystals formed from asymmetric molecules, the forces of a noncentral interaction are considerable, and the orientational order in such crystals is conserved, as a rule, even to the melting temperature [13]. The calculations performed in works [2, 11, 12] showed that the behavior of the isochoric heat conductivity of simple molecular crystals at temperatures of the order of the Debye one and higher is defined, to a great extent, by approaching the lower limiting values of heat conductivity. This effect named in [14] as the minimum of heat conductivity

is related to the restriction on the free path length of phonons. With increase in temperature, the free path length of phonons decreases, by tending to a minimum value of the order of the lattice constant. A further diminution of the free path length is impossible, and the heat conductivity, whose temperature dependence at  $T \geq \Theta_D$  is mainly determined by a decrease in the free path length of phonons, stops practically to depend on temperature, by tending to a certain minimum value. For molecular crystals, the effect of the minimum of heat conductivity can be manifested, most probably, in the region of premelting temperatures [15]. In view of the above-presented consideration, we will focus our attention on the high-temperature isobaric heat conductivity of orientationally ordered molecular crystals and analyze the influence of two determining, in our opinion, factors, namely the heat expansion and the restriction on the free path length of phonons, on its temperature dependence. It is assumed that heat is transferred in dielectric crystals by phonons which are the energy quanta of each oscillatory mode, and the free path length is determined by the energy exchange rate between phonons of different modes [4]. In the Debye model, the heat conductivity is determined by the integral

$$\Lambda = \frac{k_B}{2\pi^2 v^2} \int_0^{\omega_D} l(\omega) \omega^2 d\omega, \quad (3)$$

where  $v$  is the sound velocity (the mean value by Debye),  $\omega_D$  is the Debye frequency ( $\omega_D = (6\pi^2)^{1/3} v/a$ ), and  $l(\omega)$  is the free path length of a phonon. At  $T \geq \Theta_D$ , the free path length is mainly determined by the  $U$ -processes and, for undoped crystals, can be written as [4, 16]

$$l_u(\omega) = v/AT\omega^2. \quad (4)$$

In correspondence with the conception of the minimum of heat conductivity [17], the free path length decreases with increase in temperature, but cannot become less than the half-wavelength of a phonon  $\lambda/2$ . In this case, we cannot say, in the general case, about a phonon as the energy quantum of an elastic wave. If all oscillatory modes are scattered at a distance of the order of the half-wavelength, the heat conductivity approaches its lower bound  $\Lambda_{\min}$ . The application of the Debye formalism [18] in the case of the minimum of heat conductivity allows

us to represent relation (3) as

$$\Lambda_{\min} = \left(\frac{\pi}{6}\right)^{1/3} 2k_{\text{B}}n^{2/3}v_i \left(\frac{T}{\Theta_{\text{D}}^i}\right)^2 \int_0^{\Theta_{\text{D}}^i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx. \quad (5)$$

where  $v_i$  is the sound velocity for the polarization  $i$ ,  $\Theta_{\text{D}}^i$  is the limiting Debye frequency in Kelvin degrees ( $\Theta_{\text{D}}^i = v_i (\hbar/k_{\text{B}}) (6\pi^2 n)^{1/3}$ ), and  $n$  is the number of molecules in unit volume. We performed calculations for each type of polarization and obtained the total value of  $\Lambda_{\min}$  by summing the contributions from three oscillatory modes (two transverse ones and one longitudinal mode).

If  $(l\omega)$  becomes of the order of the wavelength of a phonon, relation (4) cannot be used for the determination of the free path length. In the region of high temperatures, the free path length of phonons is limited by a distance of the order of the half-wavelength  $\alpha\lambda/2 = \alpha\pi v/\omega$  [19], where  $\alpha$  is a numerical coefficient of the order of unity. At  $l(\omega) = \lambda/2$ , oscillations occur locally. Because the completely localized oscillations give no contribution to heat conductivity, we assume that the localization is weak, and the translational excitations of the crystal lattice can be transferred from site to site by diffusion, as it was foreseen in [19]. That is, a part of the thermal energy can be transferred by weakly localized high-frequency oscillations, “diffusive” modes. In this case, the coefficient  $\alpha$  defines a degree of deviation from the full localization. As a result, the frequency spectrum of translational oscillations of a crystal bifurcates into two branches representing the phonon (the free path length exceeds  $\alpha\lambda/2$ ) and “diffusive” (the free path length reaches the value of  $\alpha\lambda/2$ ) modes. In this case, relation (4) takes the form

$$l(\omega) = \begin{cases} v/A\omega^2 T & 0 \leq \omega \leq \omega_0, \\ \alpha\pi v/\omega = \alpha\lambda/2, & \omega_0 < \omega \leq \omega_{\text{D}}. \end{cases} \quad (6)$$

The frequency  $\omega_0$  can be determined from the relation  $v/AT\omega_0^2 = \alpha\pi v/\omega_0$  as  $\omega_0 = 1/\alpha\pi AT$ . If  $\omega_0 > \omega_{\text{D}}$ , the free path lengths for all modes exceed  $\alpha\lambda/2$ , and heat conductivity is determined exclusively by  $U$ -processes. In the case where  $\omega_0 \leq \omega_{\text{D}}$ , the integral in (3) can be separated into two parts corresponding to the contributions to the heat conductivity from low-frequency phonons  $\Lambda_{\text{ph}}$  and high-frequency “diffusive” modes  $\Lambda_{\text{dif}}$ :

$$\Lambda = \Lambda_{\text{ph}} + \Lambda_{\text{dif}}. \quad (7)$$

At temperatures of the order of the Debye one and higher ones, these contributions are equal, respectively, to

$$\Lambda_{\text{ph}} = \frac{k_{\text{B}}\omega_0}{2\pi^2 v AT}, \quad (8)$$

$$\Lambda_{\text{dif}} = \frac{\alpha k_{\text{B}}}{4\pi v} (\omega_{\text{D}}^2 - \omega_0^2). \quad (9)$$

The calculation of the parameters of isobaric heat conductivity in the frame of the given model was performed with the use of relations (7)–(9). The results of calculations are presented in Fig. 1. The necessary initial data are taken from [3,5,7]. The lacking values of sound velocities for solid  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  were calculated by the method given in [20]. The effect of heat expansion was accounted in relations (8) and (9) by means of the substitution of the values of  $v$  and  $\omega_{\text{D}}$  depending on temperature under isobaric conditions. The computer simulation was realized with the selection of values of the coefficients  $\alpha$  and  $A$  (see the Table presenting also the other values used in the calculations) in order to attain the best agreement with experimental data. The theoretical curve describes well the behavior of the temperature dependence of the isobaric heat conductivity of the substances under study, the maximum distinction from experimental data being less than 7%. The localization of high-frequency modes in solid  $\text{CO}_2$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$  begins from 105, 110, and 120 K, respectively.

The temperature intervals of existence of the solid phase of the substances studied in the present work are different, therefore, it is convenient to perform the comparison and analysis with some general unified parameter, the range of variation of which is the same for all substances. As such a parameter, we chose the reduced temperature  $\tau = T/T_m$  ( $T_m$  is the relevant melting temperature). In Fig. 2, we show the dependence of the ratio  $\omega_0/\omega_{\text{D}}$  on the reduced temperature. With increase in temperature, the ratio  $\omega_0/\omega_{\text{D}}$  decreases. Such a dependence of  $\omega_0/\omega_{\text{D}}$  is characteristic of the orientationally ordered phases of molecular crystals [15] and testifies to an increase in the contribution of “diffusive” modes to the heat transfer with increase in temperature.

The calculations of  $\Lambda_{\min}$  performed by relation (5) gave the results which are approximately, on the average, twice less than the minimum experimental values of heat conductivity (Fig. 1). Relation (5) is valid for atomic crystals and does not take the possible transfer of rotational energy between sites of the crystal lattice into account. In molecular crystals, heat is

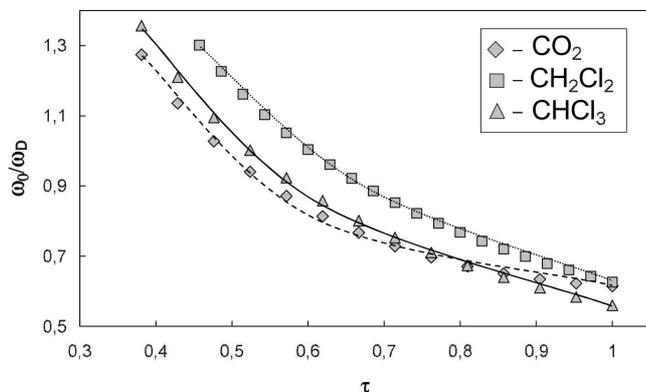


Fig. 2. Dependences of the ratio  $\omega_0/\omega_D$  on the reduced temperature

transferred by mixed translational-orientational modes, whose heat capacity at  $T \geq \Theta_D$  is saturated proportionally to the number of degrees of freedom. In view of this circumstance, the following expression for the determination of the minimum of isochoric heat conductivity of molecular crystals, whose molecules have  $z$  degrees of freedom was proposed in [15]:

$$\Lambda_{\min}^* = \frac{1}{2} \left( \frac{\pi}{6} \right)^{1/3} \left( 1 + \frac{z}{3} \right) k_B n^{2/3} (v_\ell + 2v_t). \quad (10)$$

The lower limiting values of heat conductivity obtained by relation (10) agree well with experimental data for isochoric heat conductivity [2, 15]. The results of calculations by relation (10) in the isobaric case (Fig. 1) also confirm the necessity to take the energy transfer by orientational excitations of a crystal lattice into account. The difference between the isobaric and isochoric experiments consists in the presence of heat expansion in one case and its absence in the other one. That is, the given formula accounts efficiently the effect of heat expansion and can be used in the determination of the minimum of heat conductivity both in the isochoric and isobaric cases.

### 3. Conclusions

We have shown that the temperature dependence of the isobaric heat conductivity of orientationally ordered molecular crystals at  $T \geq \Theta_D$  can be described in the Debye approximation in the frame of the model, where heat is transferred by phonon and “diffusive” modes. The performed numerical analysis indicates that the characteristic behavior of the temperature dependence of  $\Lambda_p$  of orientationally ordered crystals is mainly determined by two factors: the heat expansion and

the approach of heat conductivity to its lower limiting value. We note that the advantage of the method applied to the calculation of the heat conductivity of the orientationally ordered phases of molecular crystals consists in the possibility to use it in the absence of isochoric data, which is confirmed by the result of direct calculations.

1. O.I. Pursky, M.M. Zholonko, and V.A. Konstantinov, *Low Temp. Phys.* **29**, 771 (2003).
2. V.A. Konstantinov, V.G. Manzhelii, V.P. Revyakin, V.V. Sagan, and O.I. Pursky, *J. Phys.: Condens. Matter* **18**, 9901 (2006).
3. V.G. Manzhelii and Y.A. Freiman, *Physics of Cryocrystals* (AIP Press, New York, 1997).
4. R. Berman, *Thermal Conduction in Solids* (Clarendon Press, Oxford, 1976).
5. V.A. Konstantinov, V.G. Manzhelii, and S.A. Smirnov, *Fiz. Nizk. Temp.* **17**, 883 (1991).
6. V.A. Konstantinov, V.G. Manzhelii, and S.A. Smirnov, *Fiz. Nizk. Temp.* **14**, 749 (1988).
7. O.I. Pursky, M.M. Zholonko, and V.V. Tsibulin, *Ukr. Fiz. Zh.* **46**, 337 (2001).
8. O.I. Pursky, *J. Phys. Stud.* **9**, 337 (2005).
9. V.G. Manzhelii, A.I. Prokhvatilov, V.G. Gavrilko, and A.P. Isakina, *Handbook for Structure and Thermodynamic Properties of Cryocrystals* (Begell, Wallingford, 1999).
10. V.A. Konstantinov, V.G. Manzhelii, V.P. Revyakin, and S.A. Smirnov, *Physica B* **262**, 421 (1999).
11. O.I. Pursky, V.A. Konstantinov, and V.S. Kovtunencko, *Ukr. J. Phys.* **50**, 1261 (2005).
12. O.I. Pursky and V.A. Konstantinov, *CEPJ* **4**, 210 (2006).
13. N.G. Parsonage and L.A.K. Staveley, *Disorder in Crystals* (Clarendon Press, Oxford, 1978).
14. G.A. Slack, *Solid State Phys.* **34**, 1 (1979).
15. V.A. Konstantinov, *Fiz. Nizk. Temp.* **29**, 567 (2003).
16. P.G. Klemens, *High. Temp. – High Pressure* **83**, 249 (1983).
17. M.C. Roufosse and P.G. Klemens, *J. Geophys. Res.* **79**, 703 (1994).
18. D.G. Cahill and R.O. Pohl, *Ann. Rev. Phys. Chem.* **39**, 93 (1988).
19. D.G. Cahill, S.K. Watson, and R.O. Pohl, *Phys. Rev. B* **46**, 6131 (1992).
20. O.I. Pursky and M.M. Zholonko, *Fiz. Tverd. Tela* **46**, 1949 (2004).

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ІЗОБАРНА ТЕПЛОПРОВІДНІСТЬ  
ОРІЄНТАЦІЙНО-УПОРЯДКОВАНИХ  
МОЛЕКУЛЯРНИХ КРИСТАЛІВ

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## Резюме

На прикладі твердих  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  та  $\text{CO}_2$  проведено аналіз високотемпературної ізобарної теплопровідності орієнтаційно-

упорядкованих молекулярних кристалів. Ізобарна теплопровідність описана в рамках дебаївського наближення із врахуванням впливу теплового розширення та обмеження довжини вільного пробігу фононів. Встановлено, що температурна залежність ізобарної теплопровідності орієнтаційно-упорядкованих молекулярних кристалів при  $T \geq \Theta_D$  визначається  $U$ -процесами, тепловим розширенням дослідних зразків та наближенням теплопровідності до свого мінімального значення.