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Isochoric thermal conductivity of solid carbon oxide: the role of phonons and ‘diffusive’ modes

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Abstract

The isochoric thermal conductivity of solid CO was investigated in three samples of different densities in the interval from 35 K to the onset of melting. In α -CO the temperature dependence of the isochoric thermal conductivity is significantly weaker than $\Lambda \propto 1/T$; in β -CO it increases slightly with temperature. A quantitative description of the experimental results is given within the Debye model of thermal conductivity in the approximation of the corresponding relaxation times and which allows for the fact that the mean-free path of phonons cannot become smaller than half the phonon wavelength. On this consideration the heat is transported by both phonons and ‘diffusive’ modes.

1. Introduction

The thermal and mechanical properties of simple molecular crystals are determined by both translational and orientational motion of molecules in the lattice sites. The orientational motion can be either oscillatory or rotational depending on the relation between the noncentral force and the rotational kinetic energy. Except for rare cases (quantum crystals), the motion of molecules at rather low temperatures is essentially oscillatory: at $T \sim 0$ the molecules execute zero orientational vibrations about equilibrium directions. As the temperature rises, the root-mean-square (rms) amplitudes of the librations increase, and the molecules can jump over some accessible orientations. In some cases this may lead to a phase transition when the long-range orientational order disappears. By choosing crystals with different parameters of molecular interaction and varying the temperature, it is possible to change the degree of orientational ordering and investigate the effect of the molecule rotation upon the thermal properties, e.g. thermal conductivity of the material.

Owing to their rather simple and largely similar physical properties, N₂, CO, N₂O and CO₂ crystals, consisting of linear molecules, are suitable objects for such studies [1, 2]. In these crystals the noncentral part of the molecular interaction is determined mostly by the quadrupole forces. At low temperatures and pressures, these crystals have an fcc structure

with four molecules per unit cell. The axes of the molecules are along the body diagonals of the cube. In N_2 and CO_2 , which have equivalent diagonal directions, the space group is $Pa3$: for the noncentrosymmetrical CO and N_2O molecules the crystal symmetry is possibly described by the group $P2_13$ [1].

In CO_2 and N_2O the noncentral interaction is very strong and the long-range order persists up to their melting temperatures. In N_2 and CO the barriers impeding the rotation of the molecules are an order of magnitude lower: as a result, orientational disordering phase transitions occur at 35.7 and 68.13 K, respectively. In the high-temperature phases, the N_2 and CO molecules occupy the sites of the hcp lattice of the space group $P6_3/mmc$.

For a correct comparison with theory, the thermal conductivity must be measured at constant density to exclude the thermal expansion effect. This kind of investigation was made on CO_2 , N_2O [3] and on N_2 [4]. In the orientationally ordered phases of these crystals the thermal conductivity varied following a dependence significantly weaker than $\Lambda \propto 1/T$. It was shown that the departures occurred when the thermal conductivity was approaching its lower limit, Λ_{\min} . The concept of the lower limit of thermal conductivity implies the following [5]: Λ_{\min} is achieved when the heat transport proceeds as a diffusive exchange of thermal energy between the neighbouring quantum mechanical oscillators whose lifetime is assumed to be close to half the period of oscillations. In this case the lower limit of thermal conductivity Λ_{\min} of the lattice can be written as [5]

$$\Lambda_{\min} = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \sum_i v_i \left\{ \left(\frac{T}{\Theta_i}\right)^2 \int_0^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \right\}. \quad (1)$$

The summation is made over three (two transverse and one longitudinal) oscillatory modes having the sound velocities v_i ; Θ_i is the Debye temperature for each polarization: $\Theta_i = v_i(\hbar/k_B)(6\pi^2 n)^{1/3}$, n is the number of molecules per unit volume, $x = \hbar\omega/k_B T$. In the orientationally disordered phase of N_2 the isochoric thermal conductivity increased slightly with temperature [4]. Such behaviour was attributed to the change in the ‘rotational’ component of the total thermal resistance which decreased when the rotational correlations between the neighbouring molecules grew weaker. However, no quantitative calculation was made.

This study completes the series of investigations of the heat transport in the N_2 -type crystals. The isochoric thermal conductivity of solid CO was measured on three samples of different densities in both orientationally ordered and orientationally disordered phases. Earlier, the thermal conductivity of CO was investigated only under saturated vapour pressure in the α -phase (2–50 K) [6, 7].

2. Experimental details

Constant volume investigations are possible for molecular solids having a comparatively high compressibility coefficient. Using a high pressure cell, it is possible to grow a sample of sufficient density which in subsequent experiments can be cooled with practically unchanged volume. For samples of moderate densities the pressure drops during cooling 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 the case of a fixed volume, melting occurs in a certain temperature interval, and its onset shifts towards higher temperatures as the density of the samples increases.

This is seen, for example, in the V – T phase diagram (see figure 1) of CO based on reference literature data [1, 2]. The curve describing the phase transitions was calculated from the P – T phase diagram using averaged data $(dP/dT)_V = 3.0 \text{ MPa K}^{-1}$ for the α -phase and 2.3 MPa K^{-1} for the β -phase (the derivative of the ‘thermal’ pressure with respect

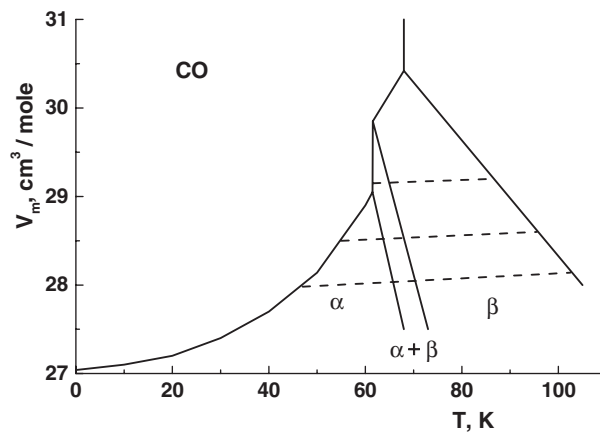


Figure 1. V - T phase diagram of solid CO. The dashed lines show the molar volumes of the samples.

to temperature $(dP/dT)_V = \beta/\chi_T$, where β is the thermal expansion coefficient, χ_T is the isothermal compressibility). It was assumed that above T_0 the ‘thermal’ pressure would grow linearly up to crossing the temperature–pressure curve along the α - β transition $P_{\alpha,\beta}(T)$; in the two-phase region the ‘thermal’ pressure changes as $P_{\alpha,\beta}(T)$. It is easy to show that the temperature interval of the existence of the two-phase region ΔT_b can be found as

$$\Delta T_b = \frac{\Delta V_f}{V} \chi_T^{-1} \left[\left(\frac{dP}{dT} \right)_f - \left(\frac{dP}{dT} \right)_V \right]^{-1} \quad (2)$$

where $\Delta V_f/V$ is the relative jump of the volume during the phase transition. The same procedure was employed to find the boundaries of the β -phase. The molar volumes of the samples plotted taking into account the thermal and elastic deformation of the measuring cell are shown in figure 1 (dashed lines).

The investigation was made using a steady-state technique in a coaxial-geometry setup [8]. The measuring beryllium bronze cell was 160 mm long with an inner diameter of 17.6 mm. The maximum permissible pressure in it was 800 MPa. The inner measuring cylinder was 10.2 mm in diameter. The temperature sensors (platinum resistance thermometers) were placed in special channels of the inner and outer cylinders and thus escaped high pressure effects. A system of protecting cylinders was used to reduce the axial heat flows. During the growth process the temperature gradient over the measuring cell was 2–3 K cm⁻¹. The pressure in the inflow capillary was varied within 50–250 MPa to grow samples of different densities. 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 their premelting temperatures to remove the density gradients. After 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 total dominant systematic error of measurement was no more than 4% for the thermal conductivity and 0.2% for the volume [8]. The purity of CO was no worse than 99.97%.

3. Results and discussion

The isochoric thermal conductivity of solid CO was investigated on three samples of different densities in the interval from 35 K to the onset of melting. The experimental results are shown

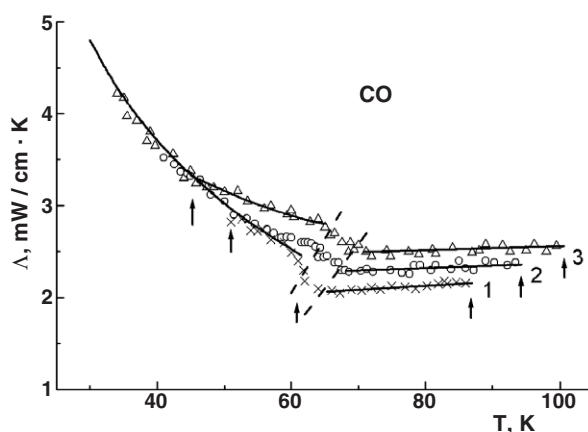


Figure 2. The isochoric thermal conductivity of three solid CO samples of different densities: 1 (\times), 2 (\circ), 3 (\triangle) (see table 1). The solid lines show the smoothed values of the thermal conductivity. The dashed lines indicate the boundaries of the two-phase α - β region. The arrows point to the onset of the $V = \text{constant}$ condition and the melting boundaries.

Table 1. Molar volumes V_m , temperatures T_0 (onset of $V = \text{constant}$ conditions), $T_{\alpha,\beta}^b$, $T_{\alpha,\beta}^e$ (beginning and end of $\alpha \rightarrow \beta$ transition) and T_m (onset of melting).

Sample	V_m ($\text{cm}^3 \text{mol}^{-1}$)	T_0 (K)	$T_{\alpha,\beta}^b$ (K)	$T_{\alpha,\beta}^e$ (K)	T_m (K)
1	29.15	61.5	61.5	65.0	92
2	28.50	55.0	64.0	68.0	96
3	27.98	44.0	65.5	70.0	102

in figure 2 (solid lines are smoothed thermal conductivity values). Our results obtained at $T \leq T_0$ correspond to the thermal conductivity at the equilibrium vapour pressure and agree with literature data [6, 7] within experimental error.

The molar volumes V_m , temperatures T_0 corresponding to the $V = \text{constant}$ condition, the temperatures $T_{\alpha,\beta}^b$, $T_{\alpha,\beta}^e$ (the beginning and end of the α - β transition, respectively) and T_m (onset of melting) are shown in table 1.

In α -CO the temperature dependence of the isochoric thermal conductivity is significantly weaker than $\Lambda \propto 1/T$ and is similar to that observed for CO_2 , N_2O and N_2 [3, 4]. In β -CO the isochoric thermal conductivity increases slightly with temperature, like in the case of N_2 [4]. Earlier, the thermal conductivity was observed to grow in orientationally disordered phases of some molecular crystals [9]. The Bridgman coefficient $g = -(\partial \ln \Lambda / \partial \ln V)_T$ calculated from the experimental results is 5.2 ± 0.5 for α -CO at $T = 60$ K and 4.0 ± 0.5 for β -CO at $T = 70$ K.

The orientational motion of the molecules in α -CO manifests itself as large-angle librations (the rms libration amplitudes are $\langle \Theta^2 \rangle^{1/2} = 14.6^\circ$ at $T = 0$ and exceed 25° immediately before the α - β transition). The librations are accompanied by hopping over a limited set of equivalent orientations interrelated by the elements of the symmetry group [1]. The frequency of reorientations obtained by extrapolating NMR [10] and dielectric permittivity [11] data is about $6 \times 10^{10} \text{ s}^{-1}$ immediately before the α - β transition (compared to 10^{11} s^{-1} in N_2) and it is no more than 10^6 s^{-1} in CO_2 and N_2O before melting [1]. Structural methods cannot provide unambiguous information about the character of orientational molecule rotation in β - N_2 and β -CO [1]. It is therefore hard to choose between the model of hindered rotation and the two

models assuming partial orientational ordering: precession about the C_6 -axis in the hexagonal lattice and hopping between the equivalent positions about this axis. The analysis of the heat capacities of β - N_2 and β -CO gives more information and reveals appreciable distinctions in their behaviour [1]. The rotational heat capacity of β -CO decreases with rising temperature, approaching asymptotically the value typical of a free rotator. In β - N_2 the heat capacity changes nonmonotonically. This behaviour corresponds conceptually to the β -phase of CO treated as a system of hindered rotators. In β - N_2 we most likely observe practically free precession of the molecules which is accompanied by axial vibrations through an angle θ with respect to the hexagonal axis of the cell [1].

Except for rare cases, the translational and orientational types of motion in molecular crystals are not independent but occur as vibrations related by the translation–orientation interaction [1]. It is impossible to describe this case with analytical expressions. Commonly, a simplified notion is used, which suggests the possibility of describing the translational and orientational subsystem independently. This approach is based on the assumption that the translation–orientation (TO) interaction leads to renormalization of the dispersion relations for rotational excitations and sound velocities [1]. In this case the thermal conductivity can be described using the expression following from the Debye model [12, 13]

$$\Lambda = \frac{\hbar^2}{2\pi^2 v^2 k_B T^2} \int_0^{\omega_D} l_\Sigma(\omega) \omega^4 \frac{\exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2} d\omega \quad (3)$$

where v is the sound velocity, ω_D is the Debye frequency, $\omega_D = v(6\pi^2 n)^{1/3}$, and $l_\Sigma(\omega)$ is the combined phonon mean free path determined by the package of all scattering mechanisms,

$$l_\Sigma(\omega) = \left(\sum_i l_i(\omega)^{-1} \right)^{-1}. \quad (4)$$

In orientationally ordered phases of molecular crystals, the phonons participating in the heat transport are scattered by both phonons and collective rotational excitations (librons). If we reduce the factors of scattering to only three quasi-particles, the mean free path limited by the Umklapp processes [13] can be found as

$$l_u(\omega) = v/A\omega^2 T. \quad (5)$$

The extra phonon scattering at librons leads to nothing but renormalization of the coefficient A as compared to pure phonon–phonon scattering [14].

In orientationally disordered phases of molecular crystals there is no long-range order, which suggests that the distinct pure libration modes cannot propagate in the crystal. Nevertheless, the correlation effects are still strong immediately after the phase transition and the short-range orientational order persists. In this region there is strong phonon scattering at the short-range orientational order fluctuations and it becomes weaker on a further temperature rise (the free molecule rotation does not lead to phonon scattering). The analytical expressions describing the mean free paths determined by one- and two-phonon scattering were obtained in the investigation of the thermal conductivity of solid methane [15]

$$l_I(\omega) = \rho v^5 / B^2 \Lambda_{\text{rot}} T \omega^2, \quad (6a)$$

$$l_{II}(\omega) = \pi \rho^2 v^8 / C^2 k_B C_{\text{rot}} T^2 \omega^4, \quad (6b)$$

where B and C are noncentral molecular interaction constants; Λ_{rot} and C_{rot} are the thermal conductivity and the heat capacity of the rotational subsystem, respectively; ρ is the density. It is assumed that $B = C^2$ in the first approximation [15]. The coefficient B can be roughly estimated from the dependence of the phase transition temperature upon pressure [15]: $B = -\chi_T^{-1} \partial(\ln T_f) / \partial P$; it is equal to 1.3. The thermal conductivity of the rotational subsystem

can be calculated from the known gas-kinetic expression: $\Lambda_{\text{rot}} = \frac{1}{3}C_{\text{rot}}a^2\tau^{-1}$, where τ is the characteristic time of the site-to-site transport of the rotational energy and can be estimated as a mean period of the librations in α -CO (we borrowed the value $\tau = 1.45 \times 10^{-13}$ s). Taking into account equations (4), (5), (6a) and (6b), the phonon mean free path in the orientationally disordered phase can be written as

$$l_{\Sigma}(\omega) = \left(\frac{AT\omega^2}{v} + \frac{B^2\Lambda_{\text{rot}}T\omega^2}{\rho v^5} + \frac{C^2k_{\text{B}}C_{\text{rot}}T^2\omega^4}{\pi\rho^2v^8} \right)^{-1}. \quad (7)$$

When the temperature rises, the phonon mean free path decreases and can become comparable with the wavelength. There has been an extensive dispute about the character of the heat transfer under these condition [5, 16–19]. According to the preferably accepted standpoint, in this case the vibrational modes become ‘diffusive’, but the basic features of the kinetic approach remain the same as they were viewed by Roufosse and Klemens [20] or by Cahill *et al* [5]. Proceeding from [5] it is possible to assume that the total mean free path is restricted to a distance close to half the phonon wavelength: $\alpha\lambda/2 = \alpha\pi v/\omega$, where α is a numerical factor of the order of unity.

$$l(\omega) = \begin{cases} l_{\Sigma}(\omega), & 0 \leq \omega \leq \omega_0, \\ \alpha\pi v/\omega = \alpha\lambda/2, & \omega_0 < \omega \leq \omega_{\text{D}}. \end{cases} \quad (8)$$

In this case the vibrational spectrum is subdivided into two parts presenting the modes whose mean free paths are larger than $\alpha\lambda/2$ (phonons) and the ‘diffusive’ modes whose mean free paths reached $\alpha\lambda/2$. In the orientationally ordered phases the ‘diffusivity’ edge ω_0 can be found from equations (5) and (8) as $\omega_0 = 1/\alpha\pi AT$. In the orientationally disordered phases ω_0 follows from equations (7) and (8):

$$\omega_0 = -\frac{u}{(-\eta + \sqrt{u^3 + \eta^2})^{1/3}} + (-\eta + \sqrt{u^3 + \eta^2})^{1/3} \quad (9)$$

where the parameters u and η are equal:

$$u = \frac{\pi\rho^2v^7}{3C^2k_{\text{B}}C_{\text{rot}}T} \left(A + \frac{B^2\Lambda_{\text{rot}}}{\rho v^4} \right), \quad \eta = -\frac{\rho^2v^7}{2\alpha C^2k_{\text{B}}C_{\text{rot}}T^2}. \quad (10)$$

The integral of thermal conductivity splits into two parts describing the contributions to the thermal conductivity from the low-frequency phonon and the high-frequency ‘diffusive’ modes:

$$\Lambda = \Lambda_{\text{ph}} + \Lambda_{\text{dif}} \quad (11)$$

where

$$\Lambda_{\text{ph}} = \frac{\hbar^2}{2\pi^2v^2k_{\text{B}}T^2} \int_0^{\omega_0} l_{\Sigma}(\omega)\omega^4 \frac{\exp\left(\frac{\hbar\omega}{k_{\text{B}}T}\right)}{\left(\exp\left(\frac{\hbar\omega}{k_{\text{B}}T}\right) - 1\right)^2} d\omega \quad (12a)$$

$$\Lambda_{\text{dif}} = \frac{\alpha\hbar^2}{2\pi vk_{\text{B}}T^2} \int_{\omega_0}^{\omega_{\text{D}}} \omega^3 \frac{\exp\left(\frac{\hbar\omega}{k_{\text{B}}T}\right)}{\left(\exp\left(\frac{\hbar\omega}{k_{\text{B}}T}\right) - 1\right)^2} d\omega. \quad (12b)$$

The applicability of this description is supported by the straightforward calculations of the thermal conductivity by the method of molecular dynamics using the Kubo–Greenwood formula. Recently, the thermal conductivity of solid argon with the Lennard-Jones potential has been described using two contributions made by low-frequency phonons with mean free paths exceeding half the wavelength and high-frequency phonons with mean free path of about half the wavelength [21].

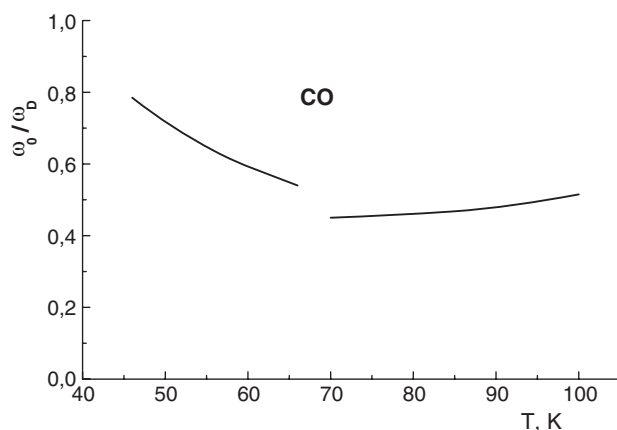


Figure 3. The ω_0/ω_D ratio upon temperature.

The lower limit of the thermal conductivity is reached when the mean free paths of all the modes are $\alpha\lambda/2$. It absolutely agrees with equation (1) if the polarization-averaged sound velocity $v = (v_l + 2v_t)/3$ and $\alpha = 1$ are used.

The results were computer-fitted by the least-square method to the smoothed values of the thermal conductivity of the highest-density sample with $V_m = 27.93 \text{ cm}^3 \text{ mol}^{-1}$ individually in the α - and β -phases. The polarization-averaged sound velocity corresponding to this density was 1280 m s^{-1} [1, 2]. It was assumed that C_{rot} varies linearly from the value $2R$ to R over the β -phase [1]. The varied parameters were α and A in the α -phase and α , A and B in the β -phase. The best agreement with the experimental results was achieved with $\alpha = 1.55$ and $A = 4.3 \times 10^{-16} \text{ s K}^{-1}$ in the α -phase and with $\alpha = 1.25$, $A = 1.0 \times 10^{-17} \text{ s K}^{-1}$, $B = 5.0$ and $C = 2.24$ in the β -phase.

The derived ω_0/ω_D ratio is shown in figure 3. As the temperature rises, the ratio ω_0/ω_D decreases in the α -phase and increases in the β -phase. This increase can be attributed to decreasing of ‘rotational’ component of the total thermal resistance, which occurs as the rotational correlations between the neighbouring molecules become weaker.

The curve fitted to the smoothed values the experimental thermal conductivity and the contributions to the thermal conductivity from low-frequency phonons Λ_{ph} and ‘diffusive’ modes Λ_{dif} calculated by equations (12a) and (12b) are shown in figure 4. It is seen that near $T = 45 \text{ K}$ most of the heat is transported by the phonons (the contribution of the ‘diffusive’ modes is no more than 10%). However, immediately before the $\alpha \rightarrow \beta$ transition over half of the heat is transported by the ‘diffusive’ modes. In the orientationally disordered phase the contribution of the ‘diffusive’ modes immediately after phase transition is about two times larger than that of the phonons. As the temperature rises, the contribution of the ‘diffusive’ modes decreases and that of the phonons increases because the scattering of the phonons by the short-range orientational order fluctuations becomes weaker due to their attenuation damping. Our estimates show that both three-phonon scattering and one-phonon scattering became the dominant mechanisms. The dotted line in figure 4 describes the lower limit of the thermal conductivity of the lattice Λ_{min}^* calculated assuming that all the modes are ‘diffusive’.

The parameters of the Debye model describing the thermal conductivity of the orientationally ordered phases of CO_2 , N_2O [3], N_2 [4] and CO are given in table 2. The computer-fitted lower limits of the thermal conductivity Λ_{min}^* are considerably higher than those calculated according to Cahill and Pohl [5]. The discrepancy can be accounted for by

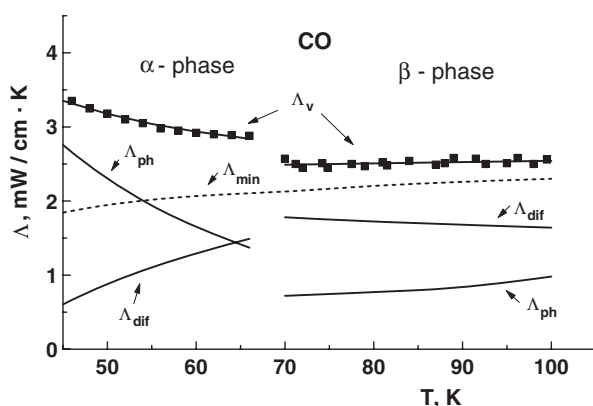


Figure 4. Results of fitting Δ_V , the smoothed values of the thermal conductivity for sample 3 and the contributions to the thermal conductivity from low-frequency phonons Δ_{ph} and ‘diffusive’ modes Δ_{dif} . The lower limit of the thermal conductivity of the lattice Δ_{min} is shown as dotted line.

Table 2. Parameters of the Debye model of thermal conductivity that used to describe the experimental results for the orientationally ordered phase (see the equations).

Substance	$n \times 10^{-22} \text{ cm}^{-3}$	$v \times 10^{-3} \text{ m s}^{-1}$	$\omega_D \times 10^{-13} \text{ s}^{-1}$	$A \times 10^{16} \text{ s K}^{-1}$	α
CO	2.15	1.28	1.38	4.3	1.55
N ₂	2.2	1.17	1.28	6.4	1.8
CO ₂	2.33	2.0	2.23	0.8	2.7
N ₂ O	2.23	1.9	2.08	1.7	2.3

the imperfection of the model. Nevertheless, there is a certain correlation between α and the number of the degree of freedom (three translational and z rotational degrees): $\alpha \propto (3 + z)/3$ for some van der Waals crystals [22] and this suggests the necessity of taking into account the site-to-site transport of the rotational energy. The method of molecular dynamics calculation of the thermal conductivity of small-pore Si-based crystals shows appreciable contributions of ‘diffusive’ optical modes to the total heat transport [23]. In CO and N₂ the coefficient α is considerably lower than that in CO₂ and N₂O. This can be because of the weaker noncentral interaction in CO and N₂ as compared to CO₂ and N₂O.

The dependence of the thermal conductivity on the molar volume can also be explained within this model. The Bridgman coefficient $g = -(\partial \ln \Delta / \partial \ln V)_T$ is the weighted mean over the phonons and ‘diffusive’ modes whose volume dependence differ considerably [22]:

$$g = \frac{\Delta_{ph}}{\Delta} g_{ph} + \frac{\Delta_{dif}}{\Delta} g_{dif}. \quad (13)$$

Equation (13) describes the general tendency of the Bridgman coefficient to decrease as more and more heat is transported by the ‘diffusive’ modes. The calculation using the procedure of [22] and the average Grüneisen coefficient $\gamma = 2.5$ for α -phase and $\gamma = 1.8$ for the β -phases [1, 2] gives $g = 5.6$ at $T = 60$ K and 4.3 at $T = 70$ K, which is in good agreement with the experimental results.

4. Conclusions

The isochoric thermal conductivity of solid CO has been investigated on three samples of different densities in the temperature interval from 35 K to the onset of melting. In α -CO the

isochoric thermal conductivity varies following a dependence rather weaker than $\Lambda \propto 1/T$. In β -CO it increases slightly with temperature. On the whole, the isochoric thermal conductivity of solid CO behaves similarly to that of solid N₂ [4]. The experimental results can be described within the Debye model of thermal conductivity in the approximation of the corresponding relaxation times and which allows for the fact that the mean-free path of phonons cannot become smaller than half the phonon wavelength. On this consideration the heat is transported by both phonons and ‘diffusive’ modes.

The contribution of the ‘diffusive’ modes becomes obvious at temperatures above 40 K. Immediately before the $\alpha \rightarrow \beta$ transition over 50% of heat is transported by ‘diffusive’ modes. In the β -phases of CO the contribution of the ‘diffusive’ modes is larger than that of the phonons and it decreases with increasing temperature, whereas the phonon contribution increases. The ratio ω_0/ω_D decreases in the α -phase and increases in the β -phase as the temperature rises. This occurs because the phonon scattering becomes weaker as the short-range orientational order fluctuations attenuate. The dependence of thermal conductivity upon density can also be adequately described within this model.

References

- [1] Manzhelii V G, Strzhemechny M A, Freiman Yu A, Erenburg A I and Slusarev V A (ed) 1996 *Physics of Cryocrystals* (New York: AIP)
- [2] Manzhelii V G, Prokhvatilov A I, Gavrilko V G and Isakina A P 1999 *Structure and Thermodynamic Properties of Cryocrystals (Handbook)* (New York: Begell House)
- [3] Konstantinov V A, Manzhelii V G and Smirnov S A 1988 *Sov. J. Low Temp. Phys.* **14** 104
- [4] Konstantinov V A, Manzhelii V G, Revyakin V P and Sagan V V 2005 *Low Temp. Phys.* **31** 419
- [5] Cahill D G, Watson S K and Pohl R O 1992 *Phys. Rev. B* **46** 6131
- [6] Koloskova L A, Krupskii I N, Manzhelii V G and Gorodilov B Ya 1973 *Sov. Phys.—Solid State* **15** 1278
- [7] Stachowiak P, Sumarokov V V, Mucha J and Jezowski A 1998 *J. Low Temp. Phys.* **111** 379
- [8] Konstantinov V A, Smirnov S A and Revyakin V P 1999 *Instrum. Exp. Technol.* **42** 133
- [9] Purskii O I, Zholonko N N and Konstantinov V A 2003 *Low Temp. Phys.* **29** 567
- [10] Walton J, Brookeman J and Rigamonti A 1983 *Phys. Rev. B* **28** 4050
- [11] Nary K R, Kuhns P L and Conradi M S 1982 *Phys. Rev. B* **26** 3370
- [12] Roufosse M and Klemens P G 1973 *Phys. Rev. B* **12** 5379
- [13] Berman R 1976 *Thermal Conduction in Solids* (Oxford: Clarendon)
- [14] Manzhelii V G, Kokshenev V B, Koloskova L A and Krupskii I N 1975 *Sov. J. Low Temp. Phys.* **1** 1302
- [15] Krupskii I N, Koloskova L A and Manzhelii V G 1974 *J. Low Temp. Phys.* **14** 403
- [16] Auerbach A and Allen P B 1984 *Phys. Rev. B* **29** 2884
- [17] Allen P B and Feldman J L 1993 *Phys. Rev. B* **48** 12581
- [18] Feldman J L, Kluge M D and Allen P B 1993 *Phys. Rev. B* **48** 12589
- [19] Sheng P, Zhou M and Zhang Z Q 1994 *Phys. Rev. Lett.* **72** 234
- [20] Roufosse M C and Klemens P G 1974 *J. Geophys. Res.* **79** 703
- [21] McGaughey A J H and Kaviany M 2004 *Heat Mass Transfer* **47** 1783
- [22] Konstantinov V A 2003 *Low Temp. Phys.* **29** 567
- [23] McGaughey A J H and Kaviany M 2004 *Heat Mass Transfer* **47** 1799