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EFFECT OF EMPTY SPACES ON THE LATTICE THERMAL CONDUCTIVITY OF POLYETHYLENE AT LOW TEMPERATURES*

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The effect of the empty spaces on the lattice thermal conductivity of polyethylene has been studied in the temperature range 0.2-5 K by calculating its total lattice thermal conductivity in the frame of its crystalline as well as non-crystalline structure. It has been found that at low temperatures, the lattice thermal conductivity of polyethylene is mainly due to its non-crystalline structure and the scattering of phonons by the empty spaces are mainly responsible for it.

Recently Saleh et al. [1, 2] studied the lattice thermal conductivity of polymers, considering their non-crystalline as well as crystalline structure, and they reported that the experimental measurements [3, 4] of the lattice thermal conductivity of a polymer can be explained well by expressing the total lattice thermal conductivity as a sum of two parts. The first part is due to the non-crystalline structure which can be estimated in the frame of the density fluctuation model, proposed by Walton [5], while the second part is due to crystalline structure, and can be calculated in the frame of the Callaway theory [6]. It is also reported that the results obtained in the frame of the above stated concepts are better than those obtained by previous workers [7—9] in the frame of the crystalline structure alone.

The studies of Saleh et al. [1, 2] indicate that at low temperature, the lattice thermal conductivity of a polymer is mainly due to the non-crystalline nature which is mainly due to scattering of phonons by empty spaces [5]. The effect of the empty spaces on the lattice thermal conductivity of a polymer has not been reported in the earlier studies. Therefore, it is interesting to see the effect of the empty spaces on the lattice thermal conductivity of a polymer. In continuation of the earlier studies, the aim of the present investigation is to study the effect of scattering of phonons by empty spaces on the lattice thermal con-

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ductivity of a polymer by calculating the total lattice thermal conductivity of polyethylene for the different values of the fraction of empty spaces. The study is made in the temperature range 0.2–5 K. It is found that below 2 K, even a small change in the empty space fraction produces a significant change in the lattice thermal conductivity. It has also been reported that the change in the lattice thermal conductivity due to a change of empty space fraction decreases as temperature increases.

According to Saleh et al. [1, 2], the total lattice thermal conductivity of a polymer can be expressed as

$$K = K_N + K_C, \tag{1}$$

where K_N is the lattice thermal conductivity due to non-crystalline structure and given by [1, 2, 5]

$$K_N = C \int_0^{\theta_c/T} (\alpha x + Bx^4)^{-1} x^4 e^x (e^x - 1)^{-2} dx, \tag{2}$$

where $C = (K_B/2\pi^2 V)(K_B T/\hbar)^3$, K_B is the Boltzmann constant, $\hbar$ is the Planck constant divided by 2π, V is the velocity of a phonon, θ_c is the characteristic temperature of the sample under study and α and B are constants, which are given by

$$\alpha = (1/4V)(K_B T/\hbar)\,[P/(1-P)], \qquad B = A' V_0 (K_B T/\hbar V)^4,$$

where the term P means the fraction of the empty spaces [5] in the polymer.

The contribution K_C is the lattice thermal conductivity due to its crystalline structure and given by

$$K_C = C \int_{\theta_c/T}^{\theta/T} (\tau_B^{-1} + \tau_{dis}^{-1} + \tau_{pt}^{-1})^{-1} x^4 e^4 (e^x - 1)^{-2} dx, \tag{3}$$

where θ is the Debye temperature of the sample under study, τ_B^{-1}, τ_{pt}^{-1} and τ_{dis}^{-1} are the scattering relaxation rates due to boundary [10], point-defects [11] and dislocations [11] respectively. Since our study is confined to low temperature only, the expression used for these scattering relaxation rates are given by

$$\tau_B^{-1} = \frac{V}{L}, \qquad \tau_{dis}^{-1} = aw = dx, \qquad \tau_{pt}^{-1} = Aw^4 = Dx^4, \tag{4}$$

where L is the Casimir length [10] of the crystal, a and A are the scattering strengths of the respective scattering processes. Thus the total lattice thermal conductivity of a polymer is given by

$$K = C\left[\int_0^{\theta_c/T} \frac{x^4 e^x (e^x-1)^{-2}}{\alpha x + Bx^4}\, dx + \int_{\theta_c/T}^{\theta} \frac{x^4 e^x (e^x-1)^{-2}}{\tau_B^{-1} + dx + Dx^4}\, dx\right]. \tag{5}$$

Using the constants reported in Table I, the lattice thermal conductivity of polyethylene has been calculated in the temperature range 0.2–5 K using Eq. (5) and the results obtained are shown in Fig. 1, which shows a very good agreement between the calculated and experi-

TABLE I

The constants used in the calculation for the lattice thermal conductivity of polyethylene in the temperature range 0.2–5 K

V (m/sec)	2.1×10^3
θ_c (K)	10
θ (K)	200
a	1×10^{-7}
B (sec^3)	1.0×10^{-42}
τ_B^{-1} (sec^{-1})	1.0×10^5
a	5.0×10^{-8}
A (sec^3)	6.0×10^{-46}
P	7.749×10^{-2}

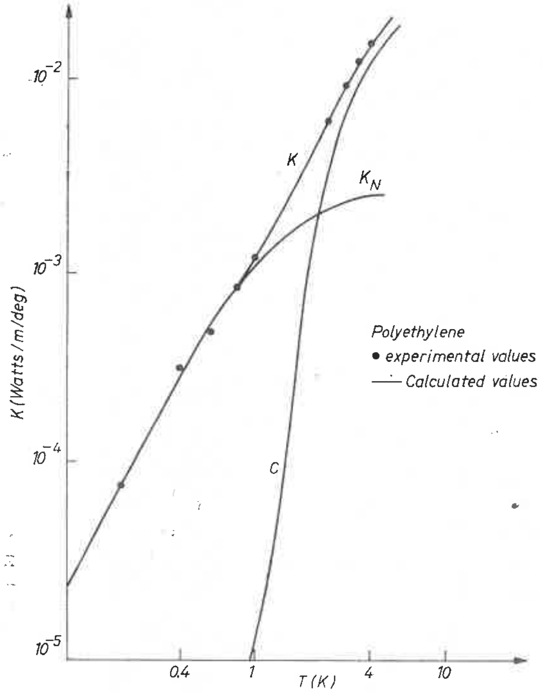

Fig. 1. The total lattice thermal conductivity of polyethylene in the temperature range 0.1–5 K. K_N is the lattice thermal conductivity due to its non-crystalline nature for $P = 0.07749$ and K_C is the same due to its crystalline structure. Circles represent the experimental points and the solid line the calculated values

mental value of the lattice thermal conductivity of polyethylene. The value of α stated in Table I corresponds to $P = 0.07749$, which shows that the fraction of the empty spaces in the present sample of the polyethylene is given by 0.07749. The fraction of empty spaces in a particular material depends on its structure.

To see the effect of the fraction of empty spaces P on the lattice thermal conductivity of a polymer, the total lattice thermal conductivity of polyethylene has been calculated in the temperature range 0.2–5 K for the different values of P such as $P = 0.2$–0.8, 0.02–0.08 and 10^{-1}–10^{-5} and the results obtained are shown in Figs 2–4. Fig. 2 shows the effect of P for its different values in the range $P = 0.2$–0.8, while Figs 3 and 4 show the effect of $P = 0.02$–0.08 and $P = 10^{-1}$–10^{-5}, respectively. The variation of the lattice thermal conductivity of polyethylene with the fraction of empty spaces P has also been shown at a different temperature in Fig. 5.

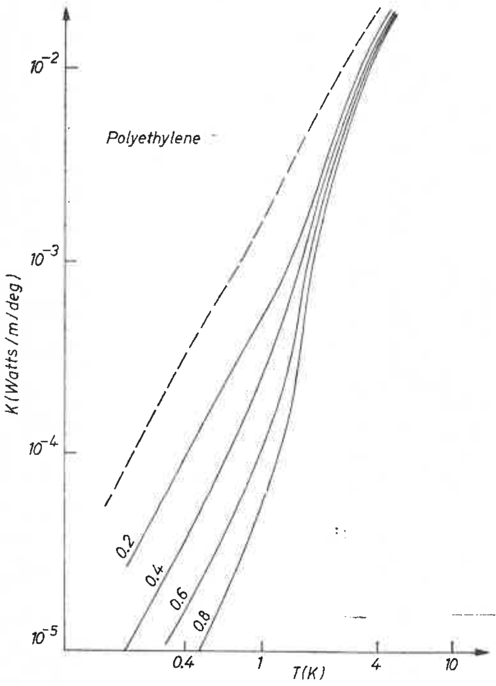

Fig. 2

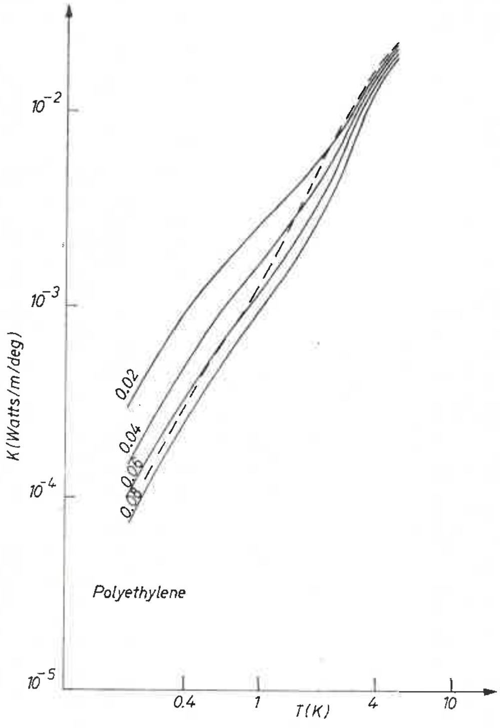

Fig. 3

Fig. 2. The total lattice thermal conductivity of polyethylene for the different values of P in the range 0.2–0.8. The value stated on the curve represents the fraction of empty spaces i.e. the value of P. The dotted line represents the lattice thermal conductivity for $P = 0.07749$ which corresponds to Fig. 1

Fig. 3. The total lattice thermal conductivity of polyethylene for the different values of P in the range 0.02–0.08. The value stated on the curve represents the fraction of empty spaces i.e. the value of P. The dotted line represents the lattice thermal conductivity for $P = 0.07749$ which corresponds to Fig. 1

The effect of the empty spaces (i.e. the parameter P) can be seen with help of Figs 2–5. With the help of Figs 2–4, it is very clear that the nature of the K vs T curve of the polyethylene is mainly assigned by the fraction of the empty spaces P. For example, from Fig. 2, it is clear that as P approaches to 0.07749 (which gives good response to the experimental data of the lattice thermal conductivity), the theoretical curve approaches to the dotted line curve (which shows the experimental data of Scott et al. [3]). At the same time, from Fig. 3, it can also be seen that as P approaches 0.1, the calculated values of the lattice thermal conductivity approach to the experimental value from the lower side. With the help of these figures as well as with the help of Fig. 5, it can be seen that at low temperature, the lattice thermal conductivity of polyethylene increases with a decrease of P at each temperature. In other words, the lattice thermal resistivity of polyethylene decreases with a decrease of empty spaces, which can be understood as below. From the earlier report of Saleh et al. [1, 2] as well as from Fig. 1, it is clear that at low temperature, the thermal conductivity of polyethylene is mainly due to its non-crystalline structure in which the scattering of phonons by empty spaces plays a dominating role. If empty spaces are less, the phonons have less resistance, hence the lattice thermal resistance has a lower value for the low value of empty spaces. This can also be explained with the help of Eq. (5). At low temperature, i.e. $\theta_c \gg T$, the second part in Eq. (5) can be neglected due to its

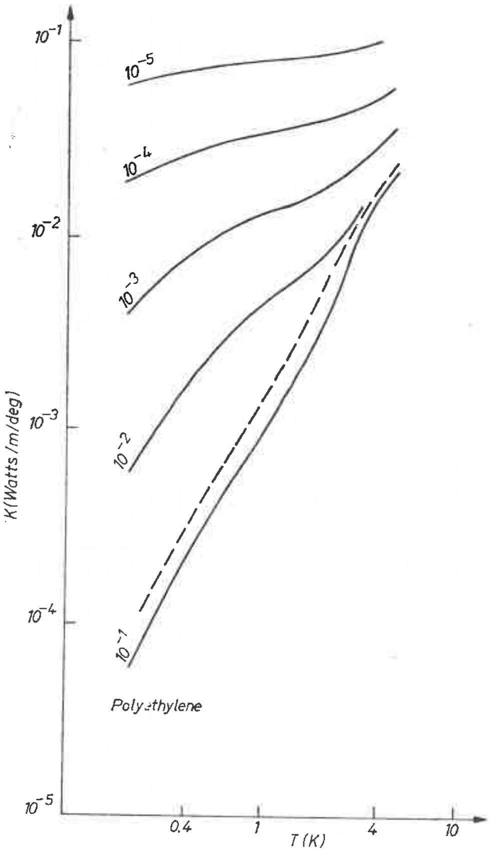

Fig. 4. The total lattice thermal conductivity of polyethylene for the different values of P in the range 10^{-1}–-10^{-5}. The value stated on the curve represents the fraction of empty space i.e. the value of P. The dotted line represents the lattice thermal conductivity for $P = 0.07749$ which corresponds to Fig. 1

small contribution and the upper limit of the first integral can be taken as ∞. Thus the total lattice thermal conductivity K can be approximated as

$$K \simeq \frac{C}{\alpha}\int_0^\infty [1+(B/\alpha)x^3]^{-1}x^3e^x(e^x-1)^{-2}dx, \tag{6}$$

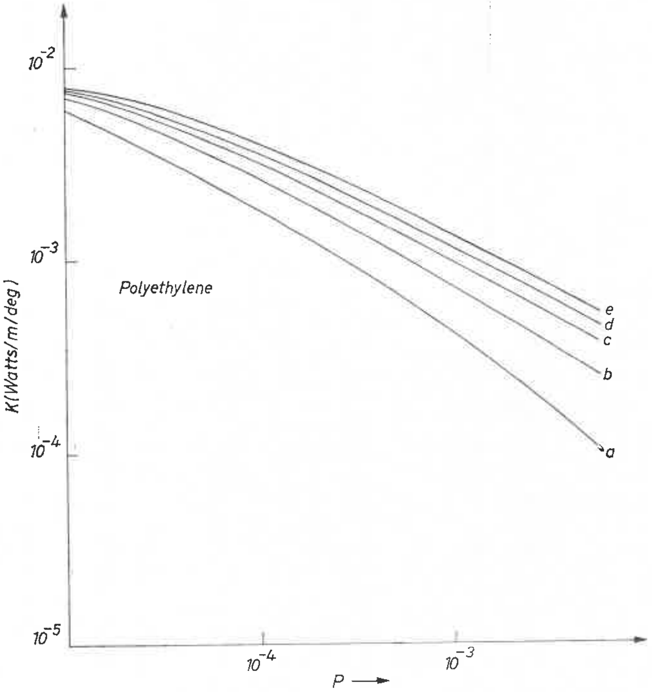

Fig. 5. The variation of the lattice thermal conductivity of polyethylene with P at a different temperature. The curves a, b, c, d and e correspond to $T = 0.2$, 0.4, 0.6, 0.8 and 1, respectively

which reduces to

$$K = 3.457\times 10^6 T^2\left(\frac{1-P}{P}\right)\left[1-9.839\times 10^{19}\frac{1-P}{P}V_0A'T^3\right],$$

which shows that K increases with a decrease of P.

Fig. 4 shows a large change in the value of the lattice thermal conductivity of polyethylene even at high temperatures. It is because of the very low value of P (which results in the domination of K_N over K_C for these values of P even at 5 K).

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