LOW TEMPERATURES LATTICE THERMAL CONDUCTIVITY OF NON- CRYSTALLINE POLYMERS
Application to polycarbonate

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Abstract

The density fluctuation model is used to analyze the lattice thermal conductivity data of two samples of polycarbonate between 0.04 and 1K. The study is carried out by calculating the lattice thermal conductivity of a noncrystalline polymer as the sum of two contributions as $K = K_{BM} + K_{EM}$, where K_{BE} is attributed to phonons which interact with the crystal boundaries, K_{EM} is due to phonons which interact with the empty spaces. The relative importance of each contribution has also been examined by estimating their percentage contributions to the lattice thermal conductivity. An excellent fit to the experimental data was obtained over the whole temperature range.

Keywords: lattice thermal conductivity, non-crystalline polymers, polycarbonate

Introduction

The lattice thermal conductivity of noncrystalline materials – including noncrstalline polymers – at low temperatures has recently attracted considerable attention. The thermal conductivity of noncrystalline polymers has been investigated by several authors [1–9] at low as well as high temperatures and it has been established for many years that the thermal conductivity of noncrystalline polymers exhibits universal behaviour below 1K, and is approximately proportional to T^2. Below room temperature, the thermal conductivity of non-crystalline materials decreases with decreasing temperature [1], and become roughly temperature independent [2] near 10 K (plateau region). At high temperatures, the thermal conductivity again increases with increasing temperature and becomes proportional to the specific heat of the sample.

Two approaches involving different phonon scattering mechanisms are used to provide an interpretation of the observed temperature dependence of the thermal conductivity of polymers. In the first approach [10, 11], the resonant scat-

tering of phonons by tunnelling states is suggested at very low temperatures, and the plateau region can be interpreted with the help of the scattering of phonons by a different band of the localized states having higher frequencies [12]. In the second approach [3, 10, 13] the scattering of phonons by empty spaces has a dominant role in the estimation of the low-temperature lattice thermal conductivity of noncrystalline polymers. This approach is known as the density fluctuation model.

Klemens [2] made the first attempt to interpret the thermal conductivity of noncrystalline materials over a wide temperature range by using the density fluctuation model and pointed out that the mean free path is proportional to the square of the phonon wave vector. Later on, Turnbull [14] pointed out that an amorphous structure has a certain fraction P of its volume which is empty and can be redistributed without change in energy. As a result of this random distribution, there will be a region which departs from the average density, leading to a scattering of phonones. Walton [13] studied the lattice thermal conductivity of noncrystalline materials in terms of the density fluctuation model proposing the scattering of phonon by empty spaces, which has been successfully applied by several workers [15–19] to explain the observed low-temperature dependence of the thermal conductivity of some polymers.

Previously, Zaitlin and Anderson [5] measured the thermal conductivity of four samples of polycarbonate in the temperature range 0.04–60 K trying to explain their measurements by using three models. They concluded that the thermal conductivity in noncrystalline materials is predominantly due to acoustic phonons. On the other hand, they could not obtain good agreement between the calculated and the experimental values of the thermal conductivity of sample P4.

For this reason, in the present work, we have also analyzed the thermal conductivity data of two samples of polycarbonate (Samples P1 & P4) in the temperature range 0.04–1 K, reported by Zaitlin and Anderson [5]. The variation of the relative contributions owing to K_{BE} and K_{EM} to the total lattice thermal conductivities of the two samples with temperature has also been studied. The variation of the scattering relaxation rates used in the present investigation with the dimensionless parameter has also been analysed at a constant temperature for the same samples.

The formula used

It has been found experimentally [20, 21], that phonons can propagate in noncrystalline materials at frequencies up to $\omega_1 = 4 \times 10^{10}$ Hz (which corresponds to temperature $T_1 = 0.4$ K) and thus contribute to the thermal transport. Following the earlier work of Walton [13] and Dubey [6] and using Debye inte-

gral, the lattice thermal conductivity of noncrystalline polymer can be expressed as the sum of three contributions as:

$$K = K_{BE} + K_{EM} + K_{AP} \tag{1}$$

$$K_{BE} = c\int_{0}^{\frac{T_1}{T}} (\mathcal{C}_B^{-1} + \alpha x T + \beta x^4 T^4)^{-1} x^4 e^x (e^x - 1)^{-2} dx \tag{2}$$

$$K_{EM} = c\int_{\frac{T_1}{T}}^{\frac{T_2}{T}} (\alpha x T + \beta x^4 T^4)^{-1} x^4 e^x (e^x - 1)^{-2} dx \tag{3}$$

$$K_{AP} = c\int_{\frac{T_2}{T}}^{\frac{\Theta_D}{T}} \beta' x^4 e^x (e^x - 1)^{-2} dx \tag{4}$$

where the contributions K_{BE}, K_{EM} and K_{AP} are attributed to phonons which have frequencies $0 < \omega < \omega_1$, $\omega_1 < \omega < \omega_{pt}$ (plateau frequency corresponding to plateau temperature, nearly 10 K) and $\omega_{pt} < \omega < \omega_D$ (Debye frequency) respectively, $c = (K_B/2\pi^2 v)(K_B/\hbar)^3$, $T_1 = \hbar\omega_1/K_B$, $T_2 = \hbar\omega_{pt}/K_B$, Θ_D is the Debye temperature, v is the average phonon velocity based on the two mode conduction [22], $\mathcal{C}_B^{-1}$ is the boundary scattering relaxation rate [23], the second term in Eq. (2) is ascribed to the scattering of phonons by empty spaces [13] while the third term corresponds to the Rayleigh scattering [24], $x = \hbar\omega/K_B T$ is a dimensionless parameter and α, β and β' are constants given in [13].

$$\alpha = 0.25(K_B\hbar)P/(1-P), \quad \beta = (A_o V_o/v^3)(K_B\hbar)^4 \quad \text{and} \quad \beta' = B_o v V_o^{1/3} \tag{5}$$

where P is the fraction of empty spaces, V_o is the critical volume, A_o and B_o are constants. It is interesting to note that at low temperatures, the contribution K_{AP} is very small [6] compared to the other types of contribution and it has been ignored in the actual calculations. Thus, the expression used for the calculation of the total lattice thermal conductivity of a noncrystalline polymer at low temperatures in the present work can be given as

$$K = c \left[\int_0^{\frac{T_1}{T}} (C_B^{-1} + \alpha xT + \beta x^4 T^4)^{-1} x^4 e^x (e^x - 1)^{-2} dx + \int_{\frac{T_1}{T}}^{\frac{T_2}{T}} (\alpha xT + \beta x^4 T^4)^{-1} x^4 e^x (e^x - 1)^{-2} dx \right]$$

(6)

Results and discussion

For a detailed analysis, the temperature dependence of the thermal conductivity data of polycarbonate samples P1 and P4 are shown in Figs 1 and 2. The study was performed by estimating the contributions K_{BE} and K_{EM} separately. Taking into account the boundary, empty spaces and Rayleigh scattering processes, the thermal conductivity data of the samples were fitted to the total lattice thermal conductivity expression with C_B^{-1}, α and β as adjustable parameters. These parameters and constants used for the fitting of different curves are listed in Table 1. Figures 3 and 4 illustrate the plot of K_{BE}/K and K_{EM}/K at different temperatures in the range 0.04–1 K for both samples. The variation of the scattering relaxation rates C_B^{-1}, αxT and $\beta x^4 T^4$ with the dimensionless parameter x
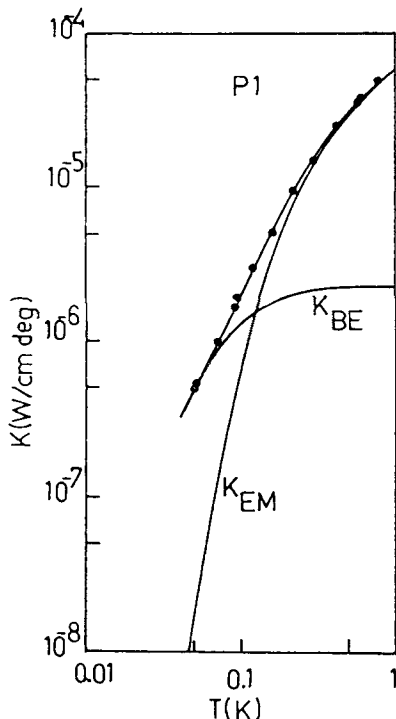

Fig. 1 Plot of the lattice thermal conductivity vs. temperature for the polycarbonate sample P1

has also been studied to examine their relative roles in the estimation of the lattice thermal conductivity of the polycarbonate samples. The results obtained are shown in Figs 5 and 6.

An excellent fit to the experimantal data, as shown by the continuous lines in Figs 1 and 2, is obtained for the whole temperature range of study. These figures show that the expression for the lattice thermal conductivity used in the present analysis gives a very good response to the experimental data of the lat-
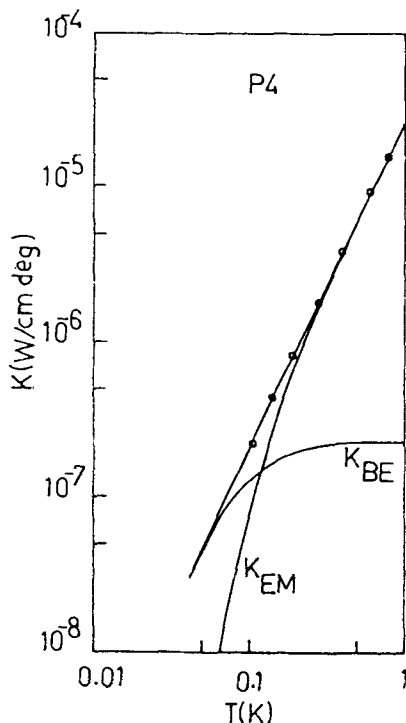

Fig. 2 Plot of the lattice thermal conductivity *vs.* temperature for the polycarbonate sample P4

Table 1 Values of the adjustable parameters determined for the polycarbonate samples P1 and P4 in the temperature range 0.04–1 K

$v/\text{m}\cdot\text{s}^{-1}$	$1.4\cdot10^3$	$1.4\cdot10^3$
$T_1/\text{ K}$	0.4	0.4
$T_2/\text{ K}$	10	10
C_B^{-1}/s^{-1}	$4.6\cdot10^6$	$1.0\cdot10^8$
$\alpha/\text{s}^{-1}\cdot\text{K}^{-1}$	$3.45\cdot10^8$	$3.2\cdot10^9$
$\beta/\text{s}^{-1}\cdot\text{K}^{-1}$	$6.3\cdot10^7$	$1.0\cdot10^5$

tice thermal conductivity of the polycarbonate at low temperatures. For temperatures almost below 0.2 K, Figs 1 and 2 make clear that the contribution K_{BE} decreases drastically with decreasing temperature, while it shows a slight decrease above this temperature.
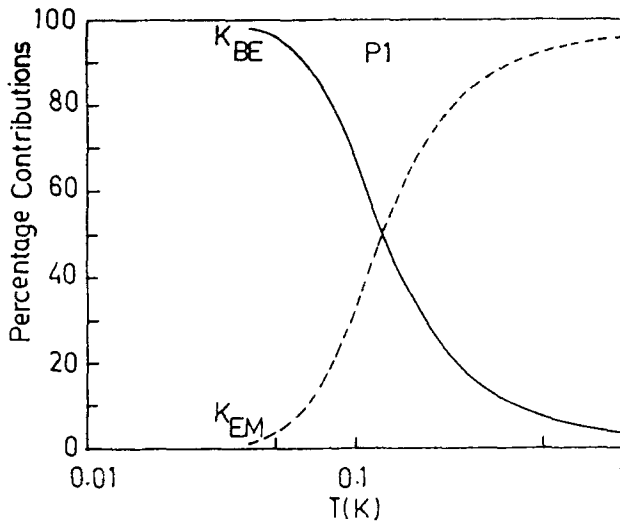

Fig. 3 Plot of the percentage contribution $\%K_{BE}$ and $\%K_{EM}$ to the total lattice thermal conductivity *vs.* temperature for the polycarbonate sample P1
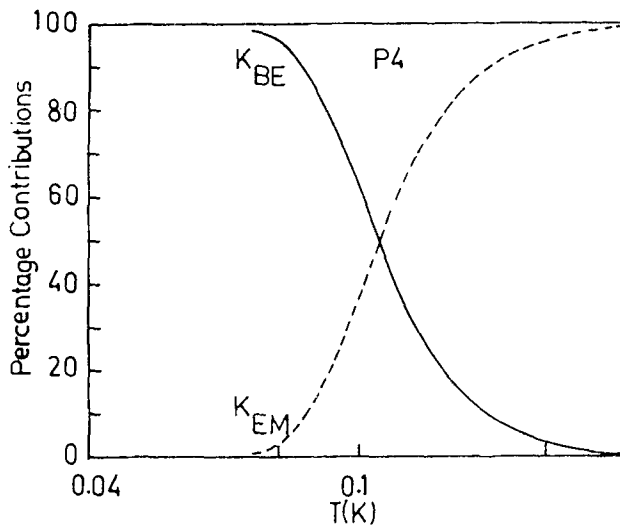

Fig. 4 Plot of the percentage contribution $\%K_{BE}$ and $\%K_{EM}$ to the total lattice thermal conductivity *vs.* temperature for the polycarbonate sample P4
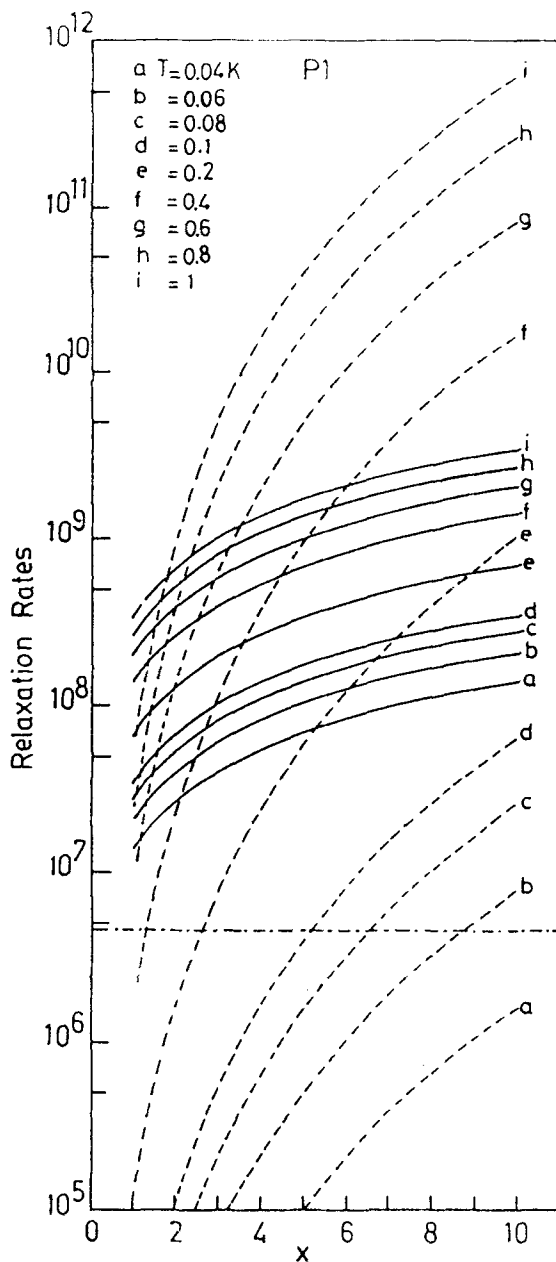
Fig 5 Plot of the scattering relaxation rates *vs.* the dimensionless parameter x for polycarbonate sample P1 for the different values of temperature. The solid lines represent $\alpha x T$, the dashed lines represent $\beta x^4 T^4$ and the dash-dotted line represents c_B^{-1}
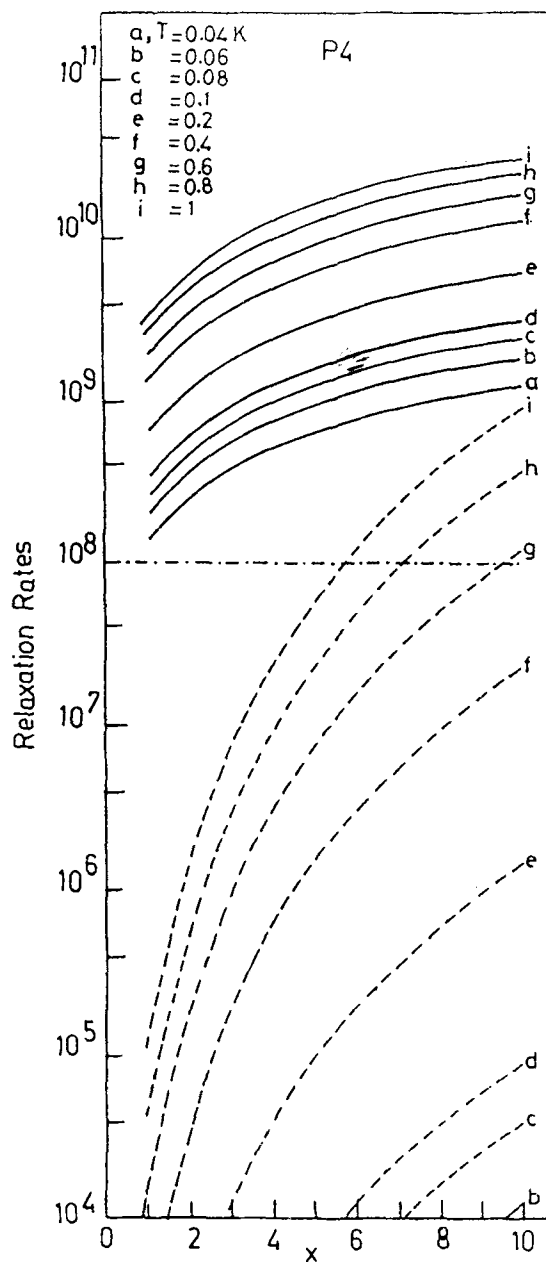
Fig 6 Plot of the scattering relaxation rates *vs.* the dimensionless parameter x for the polycarbonate sample P4 for different values of temperature. The solid lines represent $\alpha x T$, the dashed lines represent $\beta x^4 T^4$ and the dash-dotted line represents τ_B^{-1}

Figures 3 and 4 clearly demonstrate two opposite trends. At very low temperatures $\%K_{BE}$ is greater than $\%K_{EM}$, which indicates that at very low temperatures the lattice thermal resistivity of a noncrystalline polymer is mainly due to the scattering of the phonons which interact with the crystal boundary. At the same time at a little higher temperature (above 0.2 K), one can see an opposite behaviour of the percentage contribution, which means that $\%K_{EM}$ dominates over $\%K_{BE}$, and it can be said that above 0.2 K the lattice thermal resistivity is mainly due to scattering of phonons by empty spaces. As a result one can conclude that at low temperatures, the total lattice thermal conductivity of a noncrystalline polymer is mainly due to the contribution K_{EM} in which the scattering of phonons by empty spaces plays an important role.

Figure 5 reveals that just below 0.2 K, the empty space scattering relaxation rate (αxT) dominates over the Rayleigh scattering relaxation rate $(\beta x^4 T^4)$, while above this temperature, it shows an opposite nature so that the term $\beta x^4 T^4$ dominates over αxT for large values of the dimensionless parameter x. It should also be noted that at very low temperatures and for low values of the dimensionless parameter x, the boundary scattering relaxation rate C_B^{-1} dominates over other types of scattering relaxation rates. However, it would be instructive to note the importance of the boundary scattering relaxation rate C_B^{-1} at very low temperatures. By examining the curves in Fig. 6 for the polycarbonate sample P4, it becomes quite clear that the empty space scattering relaxation rate is much larger than other scattering relaxation rates, which reflects the effectiveness of the empty space scattering at low temperatures. It is also clear that below 0.6 K, the boundary scattering relaxation rate is larger than the Rayleigh scattering relaxation rate for all values of the dimensionless parameter.

Conclusions

From the foregoing, the following conclusions can be drawn:

1. The lattice thermal conductivity of a noncrystalline polymer has been studied at low temperatures by considering the separate contribution of K_{BE} and K_{EM}, and a very good agreement has been found between the predicted and observed lattice thermal conductivity, and the expression proposed in Eq. (6) could successfully explain the experimental data.

2. The percentage contribution $\%K_{BE}$ dominates over $\%K_{EM}$ below a certain temperature (say about 0.1 K), and the opposite is also true above that temperature. In other words, the percentage contribution $\%K_{BE}$ decreases with increasing temperature, an opposite trend is shown for $\%K_{EM}$ with temperature. At the same time one can conclude that most of the heat is transported by phonons that have frequencies $\omega_1 < \omega < \omega_{pt}$.

3. The relative importance of the different scattering ralaxation rates showns that the scattering of phonons by empty spaces plays a very important role in the calculation of the lattice thermal resistivity and the boundary scattering relaxation rate cannot be ignored in the low-temperature lattice thermal conductivity.

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Zusammenfassung — Das Dichteschwankungsmodell wurde zur Analyse der Gitterwärmeleitfähigkeitsdaten von zwei Polykarbonatproben zwischen 0,04 und 1 K angewendet. Dabei wird die Gitterleitfähigkeit eines nichtkristallinen Pulvers als Summe $K = K_{BM} + K_{BE}$ aus zwei Komponenten berechnet, wobei K_{BE} Phononen zugeordnet wird, die in Wechselwirkung mit den Kristallgrenzen treten, K_{EM} gehört zu Phononen, die mit dem Leerraum in Wechselwirkung treten. Die relative Bedeutung ihres Beitrages wurde auch durch eine Schätzung ihres prozentuellen Beitrages zur Gitterwärmeleitfähigkeit geprüft. Im gesamten Temperaturbereich konnte eine ausgezeichnete Übereinstimmung mit den experimentellen Angaben beobachtet werden.