

DEGREE OF CRYSTALLINITY AND LATTICE THERMAL CONDUCTIVITY OF POLYETHYLENE AT LOW TEMPERATURES

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Abstract

The lattice thermal conductivity of a semicrystalline polymer was studied at low temperatures by calculating the total lattice thermal conductivities of four samples of polyethylene with different degrees of crystallinity between 0.43 and 0.81 and temperatures between 0.4 and 20 K. The contributions of the crystalline and noncrystalline natures and their percentage contributions were taken into account. The predicted lattice thermal conductivity of polyethylene was in fairly good quantitative agreement with the experimental value, and showed a strong crystallinity dependence, with a distinctive cross-over point at about 2 K.

Keywords: polymer, polyethylene, thermal conductivity

Introduction

Many experimental and theoretical studies [1–12] have been conducted to investigate the thermal conductivities of amorphous and semicrystalline polymers. It is well known that the thermal conductivities of amorphous materials, whether organic or inorganic, display similar temperature dependences [13]. In the temperature region below 0.5 K, the lattice thermal conductivity of a noncrystalline polymer is approximately proportional to T^2 . As the temperature increases, this conductivity increases more slowly, and between 5 and 15 K, it becomes almost independent of temperature (plateau region). The lattice thermal conductivity again increases at high temperatures and becomes proportional to the specific heat at about 60 K. The plateau region has not been observed in the measurement of the lattice thermal conductivities of semicrystalline polymers, and the temperature dependence of the lattice thermal conductivity is vastly different from that for amorphous polymers. At the same time, the temperature dependence of the lattice thermal conductivity of a semicrystalline polymer is also different from that of the crystalline polymer. Below

20 K, it is observed that the lattice thermal conductivity exhibits T and T^3 temperature dependences, as well as a strong dependence upon the degree of crystallinity.

In their attempts to analyze the experimental data on the lattice thermal conductivity of a polymer, some of the earlier workers [1, 2] assigned a two-dimensional frequency distribution function for phonon frequencies less than the critical frequency ω_c and a three-dimensional frequency distribution for frequencies greater than ω_c . Choy and co-workers [9, 10] assumed that the semicrystalline polymer is composed of crystalline lamellae embedded in an amorphous matrix. It has been found [14–17] that at very low temperatures the temperature dependence of the lattice thermal conductivity of a semicrystalline material is similar to that of a polymer. In a semicrystalline polymer, phonons are scattered by a combination of two processes. The first is the scattering of phonons by the internal boundaries, which is characterized by a frequency-independent mean free path, while the second is due to the structure scattering, which can be studied by the density fluctuation model as proposed by Klemens [18] and by Walton [19]. According to Assfalg [20], the scattering relaxation rate can be expressed as the sum of two relaxation rates, arising from the amorphous phase and spherulites in the polymer. Considering the crystalline and noncrystalline natures of a semicrystalline polymer, Dubey and co-workers [21–23] expressed the total lattice thermal conductivity as the sum of two parts. The first is attributed to the noncrystalline structure, which can be estimated by using the density fluctuation model proposed by Walton [19], while the second is related to the crystalline structure and can be calculated in the frame of the Callaway theory [24].

The present investigation comes as a continuation of the earlier studies. Its objective is the study of the lattice thermal conductivities of four samples of polyethylene in the temperature range 0.4–20 K. This material was selected as the subject of this work due to its crystallinity, which can be changed over a wide range (0.43 to 0.81) where relevant data are available. Thus, one can have a number of samples of polyethylene with different degrees of crystallinity without change in the chemical composition. The study was performed by estimating the contributions of the crystalline (K_C) and noncrystalline (K_N) natures separately. The effects of the degree of crystallinity on the contributions of the crystalline and noncrystalline natures are likewise reported in the present study. The relative importance of each type of contribution was also studied by calculating its percentage contribution to the total lattice thermal conductivity.

Expression for the lattice thermal conductivity

Empirically, it is known from ultrasonic [25] and light scattering [26, 27] experiments that phonons propagate in amorphous materials at frequencies up to $\omega_1=4 \cdot 10^{10}$ Hz, and hence contribute to the thermal resistivity of the material by interacting with the crystal boundaries. Thermal phonons in this frequency range correspond to temperatures ≈ 0.4 K. Considering the contributions of crystalline and noncrystalline natures, the total lattice thermal conductivity of a semicrystalline polymer can be given as

$$K = K_N + K_C \quad (1)$$

Density fluctuations have previously been considered by Klemens [18], who gave a phenomenological treatment yielding a phonon mean free path proportional to q^2 , where q is the phonon wave vector. This treatment holds true when the wavelength is much smaller than the correlation length L , while in the opposite limit the mean free path is constant. Ziman [28] suggested that the correct formula would contain both cases. Later, Walton [19] supposed that the amorphous structure has a certain fraction P of its volume empty, this fraction P giving rise to phonon scattering. According to Walton [19] the expression for the mean free path becomes:

$$l^{-1}(q) = \frac{1}{4} \frac{P}{1-P} q + A_0 q^4 V_0 \quad \text{for } qV_0^{1/3} < 1 \quad (2)$$

$$l^{-1}(q) = B_0 V_0^{1/3} \quad \text{for } qV_0^{1/3} > 1 \quad (3)$$

where P is the fraction of empty spaces, which depends on the thermal history of the sample, A_0 and B_0 are constants, and V_0 is the critical volume. The first term on the right-hand side of Eq. (2) represents the scattering of phonons by empty spaces, while the second term corresponds to the Rayleigh scattering [29].

As mentioned earlier, the phonons with a frequency range $0 < \omega < \omega_1$ can interact with the crystal boundaries and the empty spaces, while the phonons with frequency range $\omega_1 < \omega < \omega_{pt}$ (plateau frequency corresponding to plateau temperature) can interact with empty spaces only. The phonons having a frequency range $\omega_{pt} < \omega < \omega_D$ (Debye frequency) can not interact with either the crystal boundaries or the empty spaces. Following the earlier work of Dubey [22, 23] and using (2) and (3), the combined scattering relaxation rates corresponding to the three different frequency ranges can be given by:

$$\mathcal{C}_{BE}^{-1} = \mathcal{C}_B^{-1} + \alpha xT + \beta x^4 T^4 \quad \text{for } 0 < \omega < \omega_1 \quad (4)$$

$$\mathcal{C}_{EM}^{-1} = \alpha xT + \beta x^4 T^4 \quad \text{for } \omega_1 < \omega < \omega_{pt} \quad (5)$$

$$\mathcal{C}_{AP}^{-1} = \beta', \quad \text{for } \omega_{pt} < \omega < \omega_D \quad (6)$$

where \mathcal{C}_B^{-1} is the boundary scattering relaxation rate [30], α , β and β' are constants and can be calculated with the help of (2) and (3) as:

$$\alpha = \frac{1}{4} \frac{P}{1-P} \frac{K_B}{\hbar} \quad (7)$$

$$\beta = \frac{A_0 V_0}{v^3} \left(\frac{K_B}{\hbar} \right)^4 \quad (8)$$

$$\beta' = bvV_0^{-1/2} \quad (9)$$

where v is the phonon velocity. If the combined scattering relaxation rates and their respective frequency ranges are considered and the Dubey integral is used, the lattice thermal conductivity of the noncrystalline nature of a semicrystalline polymer can be expressed as:

$$K_N = K_{BE} + K_{EM} + K_{AP} \quad (10)$$

$$K_N = c \left[\int_0^{T_1/T} \mathcal{C}_{BE} J(x) dx + \int_{T_1/T}^{T_2/T} \mathcal{C}_{EM} J(x) dx + \int_{T_2/T}^{\theta_D/T} \mathcal{C}_{AP} J(x) dx \right] \quad (11)$$

where $c = (K_B/2\pi^2 v)(K_B/\hbar)^3$, $J(x) = x^4 e^x (e^x - 1)^{-2}$, $T_1 = \hbar\omega_1/K_B$, $T_2 = \hbar\omega_{pv}/K_B$ and θ_D is the Debye temperature. At low temperatures, the contribution K_{AP} is negligibly small as compared with the other types of contribution.

When the Callaway [24] expression for the lattice thermal conductivity is used, the contribution K_C due to the crystalline nature of a semicrystalline polymer can be given by:

$$K_C = c \int_{T_2/T}^{\theta_D/T} (\mathcal{C}_B^{-1} + \mathcal{C}_{dis}^{-1} + \mathcal{C}_{pt}^{-1} + \mathcal{C}_{ph}^{-1})^{-1} J(x) dx \quad (12)$$

where \mathcal{C}_{dis}^{-1} , \mathcal{C}_{pt}^{-1} and \mathcal{C}_{ph}^{-1} are the dislocation [31], point defect [31] and phonon-phonon [32] scattering relaxation rates, respectively. The expressions used

for these scattering relaxation rates are given by $C_{dis}^{-1} = a\omega$, $C_{pt}^{-1} = A\omega^4$ and $C_{ph}^{-1} = B\omega^2 T^3$, where a , A and B are the scattering strengths of the respective processes.

Thus, the total lattice thermal conductivity of a semicrystalline polymer at low temperature can be written as:

$$K = c \left[\int_0^{T_1/T} (C_B^{-1} + \alpha x T + \beta x^4 T^4)^{-1} J(x) dx + \int_{T_1/T}^{T_2/T} (\alpha x T + \beta x^4 T^4)^{-1} J(x) dx + \int_{T_2/T}^{\theta_p/T} (C_B^{-1} + Gx + Dx^4 + bx^2)^{-1} J(x) dx \right] \quad (13)$$

where $G = a(K_B T / \hbar)$, $D = A(K_B T / \hbar)^4$ and $b = B(K_B / \hbar)^2 T^5$.

Lattice thermal conductivity of polyethylene

Kolouch and Brown [4] measured the thermal conductivities of four samples with crystallinities in the range from 0.43 to 0.81 between 1.2 and 20 K. Scott *et al.* [2] also measured the thermal conductivity of polyethylene in the temperature range 0.15–4 K and attempted to explain their results in the frame of two- and three-dimensional approaches. Dubey [11] set out to explain the data of Scott *et al.* by considering the presence of both core and strain field dislocations in the crystalline structure. Saleh *et al.* [21, 23] analysed the above measurements by estimating the contributions of crystalline and noncrystalline structures.

By adjustment of the strengths of the different scattering processes (Table 1), the total lattice thermal conductivities of the four samples of polyethylene at the different degrees of crystallinity $X = 0.43, 0.56, 0.71$ and 0.81 were calculated between 0.4 and 20 K by estimating the separate contributions of K_N and K_C with the help of (13). Results obtained are shown in Fig. 1. The experimental data on the lattice thermal conductivity of polyethylene are taken from the report of Kolouch and Brown [4]. The variation in the total lattice thermal conductivity with the degree of crystallinity X at a constant temperature is likewise illustrated in Fig. 2.

The variations in K_N and K_C with temperature for different values of crystallinity X are shown in Figs 3 and 5, while the variations in K_N and K_C with the degree of crystallinity X at a constant temperature are reported in Figs 4 and 6. The effects of the degree of crystallinity X on the contributions of noncrystalline and crystalline structures were also studied by calculating the separate percent-

Table 1 Values of parameters used for theoretical curves

	X=0.43	X=0.56	X=0.71	X=0.81
T_1 / K	0.4	0.4	0.4	0.4
T_2 / K	10	10	10	10
θ / K	135	135	135	135
$\nu / 10^5 \text{ cm}\cdot\text{s}^{-1}$	1.98	2.01	2.17	2.26
$\alpha / 10^9 \text{ s}^{-1}\cdot\text{K}^{-1}$	0.8	0.85	0.85	0.9
$\beta / 10^7 \text{ s}^{-1}\cdot\text{K}^{-1}$	2.8	3.0	3.5	4.0
a	0.115	0.08	0.045	0.02
$A / 10^{-40} \text{ s}^3$	0.77	0.75	0.3	0.08
$C_B^{-1} / 10^5 \text{ s}^{-1}$	1.0	1.0	1.0	1.0
$B / 10^{-25} \text{ s}\cdot\text{K}^3$	1.0	1.0	1.0	1.0

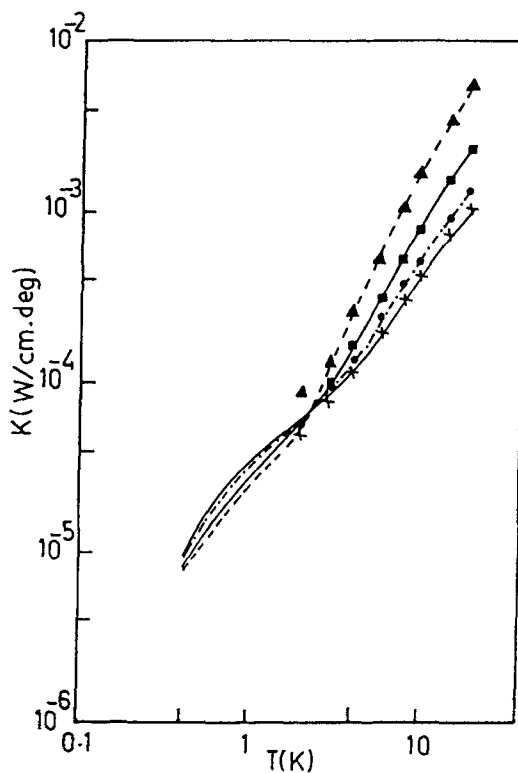


Fig. 1 Lattice thermal conductivity of four samples of polyethylene. Solid lines are the calculated values. \blacktriangle , \blacksquare , \bullet and \times are the observed values corresponding to samples having different degrees of crystallinity, $X=0.43$, 0.56 , 0.71 , 0.81 respectively

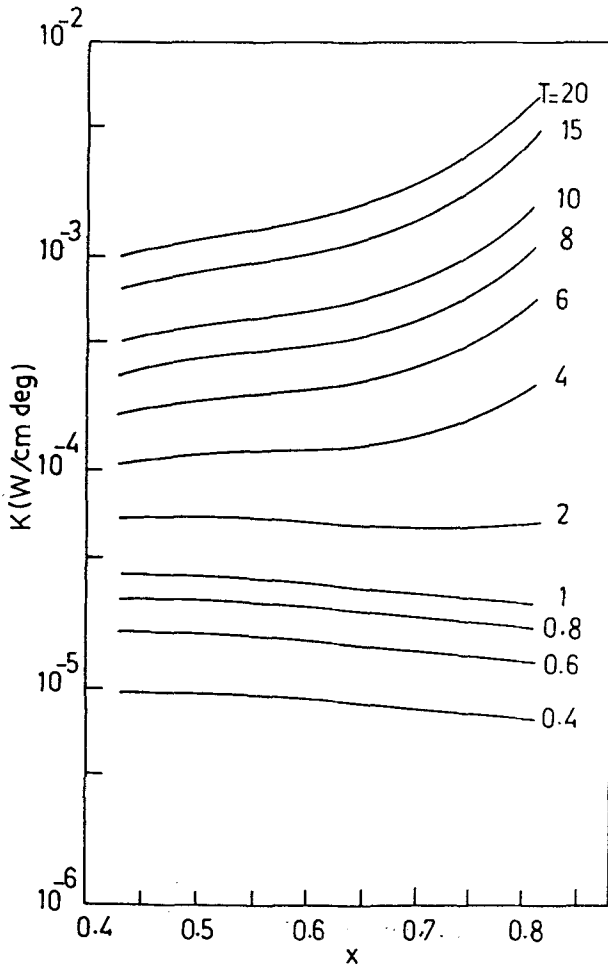


Fig. 2 Variation of the lattice thermal conductivity of polyethylene with the degree of crystallinity X at constant temperature

age contributions $\%K_N$ ($\%K_{BE} + \%K_{EM}$) and $\%K_C$ for each sample. The results obtained are listed in Table 2.

Results and discussion

In Fig. 1, the predicted and available observed lattice thermal conductivities of four samples of polyethylene are depicted against temperature. For temperatures above 2 K, a marked accord may be observed between the theoretical values and the available experimental data. It can also be seen that in this range of temperatures the lattice thermal conductivity of polyethylene increases with in-

Table 2 The percentage contribution % K_{BE} , % K_{EM} and % K_C towards the total lattice thermal conductivity of polyethylene

T / K	X = 0.43			X = 0.56			X = 0.71			X = 0.81		
	% K_{BE}	% K_{EM}	% K_C	% K_{BE}	% K_{EM}	% K_C	% K_{BE}	% K_{EM}	% K_C	% K_{BE}	% K_{EM}	% K_C
0.4	7.499	92.501	0	7.505	92.495	0	7.638	92.362	0	7.702	92.298	0
0.5	6.329	93.671	0	6.398	93.602	0	6.695	93.305	0	7.098	92.902	0
0.6	4.022	95.978	0	4.049	95.951	0	4.186	95.814	0	4.253	95.747	0
0.7	3.297	96.700	0.003	3.336	96.670	0.004	3.413	96.590	0.007	3.515	96.464	0.018
0.8	2.814	97.174	0.012	2.850	97.150	0.018	2.910	97.057	0.033	2.979	96.940	0.081
0.9	2.458	97.504	0.038	2.493	97.450	0.057	2.588	97.305	0.107	2.646	97.094	0.260
1	2.162	97.743	0.095	2.198	97.658	0.144	2.286	97.445	0.269	2.344	97.000	0.656
2	1.213	93.427	5.360	1.188	90.840	7.972	1.173	84.623	14.204	1.018	69.951	29.031
3	0.878	80.022	19.100	0.796	72.682	26.522	0.695	58.255	41.050	0.435	36.194	63.371
4	0.664	64.846	34.490	0.564	54.893	44.543	0.432	38.668	60.900	0.232	20.247	79.521
5	0.512	51.827	47.661	0.412	41.527	58.061	0.284	26.741	72.975	0.139	12.747	87.114
6	0.403	41.665	57.932	0.312	32.100	67.588	0.206	19.454	80.340	0.083	8.771	91.146
7	0.325	33.970	65.705	0.245	25.481	74.274	0.155	14.800	85.045	0.077	6.429	93.494
8	0.267	28.181	71.552	0.198	20.757	79.045	0.122	11.678	88.200	0.054	4.928	95.018
9	0.224	23.764	76.012	0.164	17.303	82.533	0.098	9.502	90.400	0.042	3.907	96.051
10	0.191	20.364	79.445	0.139	14.720	85.141	0.082	7.928	91.990	0.035	3.248	96.717
15	0.106	11.411	88.483	0.077	8.196	91.727	0.042	4.148	95.810	0.017	1.615	98.368
20	0.076	7.950	91.974	0.054	5.767	94.179	0.029	2.820	97.151	0.011	1.038	98.952

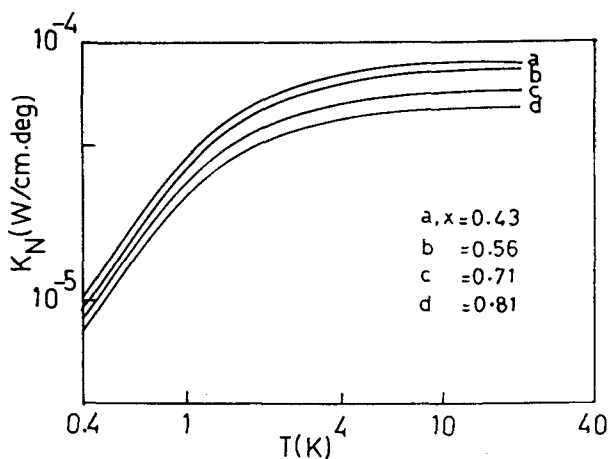


Fig. 3 The contribution to the lattice thermal conductivity due to noncrystalline structure for the different values of degree of crystallinity X

creasing degree of crystallinity, but this effect diminishes near 2 K, while an opposite trend can be seen in the range $T < 2$ K with a crossover near 2 K. However, close examination of the points observed for the samples considered in Fig. 1 reveals the existence of a crossover especially for the samples with degrees of crystallinity $X=0.43$ and 0.71 . The increase in the lattice thermal conductivity with increasing degree of crystallinity can be accounted for by the reflection of the higher average conductivity of the crystalline structure.

Choy and Greige [33] assumed that the difference in elastic properties between the crystalline and amorphous regions gives rise to a thermal boundary resistance. As the temperature decreases, the boundary resistance increases, so that near a certain temperature, the contribution of the thermal boundary resistance predominates over any increase in conductivity due to the presence of the crystalline region, consequently leading to the crossover in the thermal conductivity curves. The crystalline material has a higher average conductivity than the amorphous material, so that at high temperature, where the boundary resistance is negligible, the net conductivity of a polymer increases as the degree of crystallinity increases.

A better illustration is provided by the data on polyethylene terephthalate (PET) [33], which clearly demonstrate two opposite trends. At low temperatures, the percentage contribution $\%K_N$ is greater than $\%K_C$ (Table 2). This indicates the effect of the presence of the available scattering processes in the noncrystalline part, which involve boundary scattering and empty space scattering. At the same time, $\%K_{EM}$ is much larger than $\%K_{BE}$, which shows that the

low-temperature lattice thermal resistivity of the noncrystalline structure is mainly due to the scattering of phonons by the empty spaces.

Saleh and Dubey [34] showed that below 1 K, the lattice thermal conductivity of polyethylene is almost independent of the boundary scattering relaxation rate. They also demonstrated [22] that at low temperature the lattice thermal conductivity of polyethylene decreases with increasing P (fraction of empty space), which reflects the effectiveness of empty space scattering. Table 1 reveals that the value of P increases as the degree of crystallinity increases. This means that at low temperature there is an increasing degree of crystallinity, increasing P , and hence decreasing lattice thermal conductivity. The crossover behaviour can therefore be interpreted at low temperatures, as a result of the predominance of the influence of the value of P over any increase in thermal

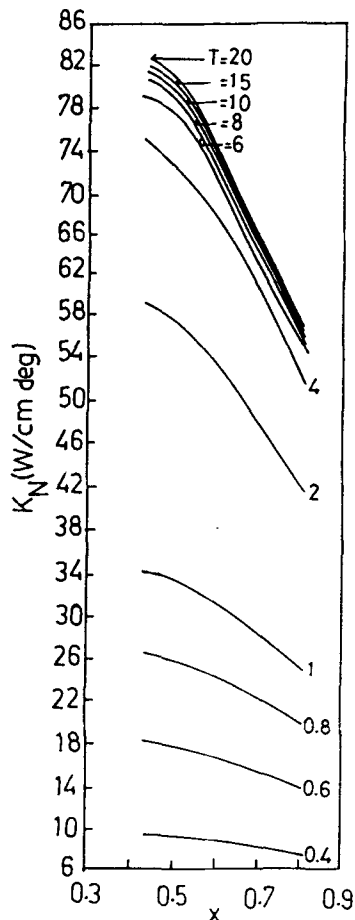


Fig. 4 Variation of the contribution K_N with the degree of crystallinity X at constant temperature

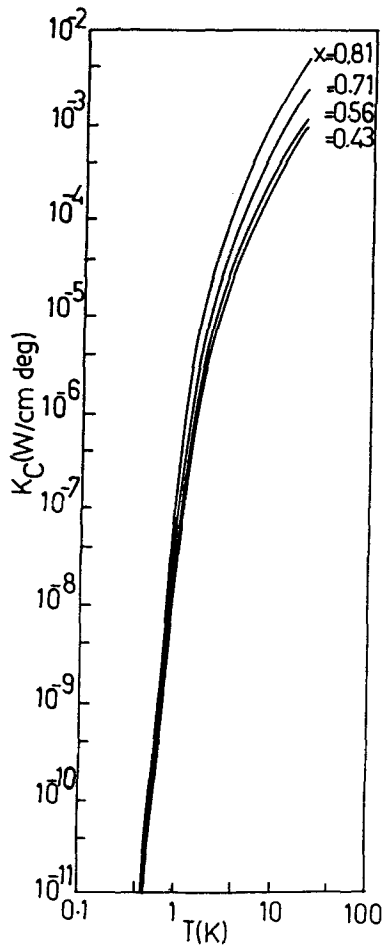


Fig. 5 The contribution to the lattice thermal conductivity due to crystalline structure for the different values of degree of crystallinity

conductivity that comes from the degree of crystallinity. From Table 2, it can also be seen that $\%K_N$ decreases with increasing temperature and degree of crystallinity, while $\%K_C$ exhibits an increasing nature in the temperature range of this study. Below a certain temperature (which varies according to the degree of crystallinity), $\%K_N$ predominates over $\%K_C$, while the reverse holds above that temperature. Table 2 shows a zero contribution due to K_C at very low temperatures. In fact, it is not zero, but the value is so small that it can be considered zero.

Figure 2 illustrates that the lattice thermal conductivity below 2 K decreases as the degree of crystallinity X increases, whereas above this temperature it dis-

plays an increasing tendency with increasing degree of crystallinity. From Figs 3 and 4, it can be said that K_N shows an increasing tendency with increasing temperature, while it decreases with increasing degree of crystallinity. Just below 4 K, it can be seen that for each degree of crystallinity the contribution K_N changes rapidly downward, while above this temperature it shows a very slow variation with temperature. It is very clear that the natures of the K_N vs. T curves are similar for all the samples considered. Figures 5 and 6 demonstrate that the contribution K_C increases with increasing T and increasing degree of crystallinity X , and the natures of K_C vs. X are very similar at each temperature in the range of study.

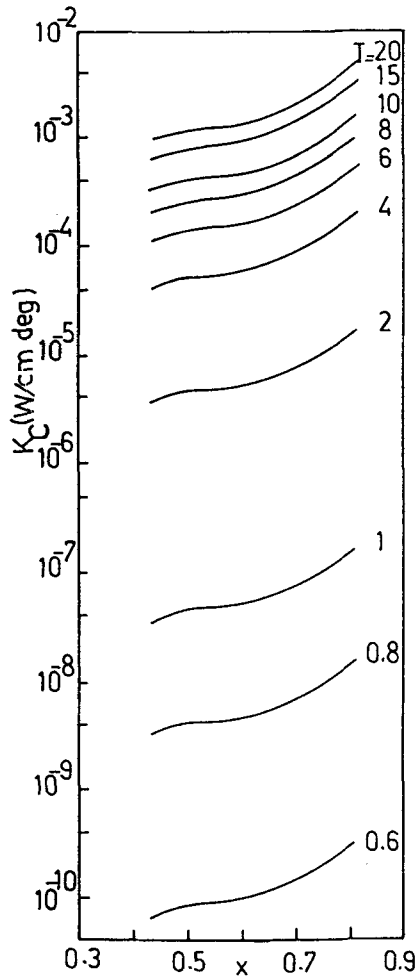


Fig. 6 Variation of the contribution K_C with the degree of crystallinity X at constant temperature

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Zusammenfassung — Die Gitterwärmeleitfähigkeit eines semikristallinen Polymers wurde bei niedrigen Temperaturen über die Berechnung der gesamten Gitterwärmeleitfähigkeit von vier Proben aus Polyethylen mit verschiedenem Kristallinitätsgrad zwischen 0,43 und 0,81 und bei Temperaturen zwischen 0,4 und 20 K untersucht. Dabei wurde der Beitrag des kristallinen und nichtkristallinen Natur und ihr prozentueller Beitrag berücksichtigt. Die vorausgesagte Gitterwärmeleitfähigkeit von Polyethylen stand in guter quantitativer Übereinstimmung mit dem experimentellen Wert, und zeigt eine starke Kristallinitätsabhängigkeit mit einem auffälligen Cross-over bei etwa 2 K.