1. See Fig. 1 on p. 387.

[12] D. N. Zubarev, Usp. Fiz. Nauk 71, (1960) [translation: Sov. Phys.-Uspekhi 3, 320 (1969)]. Equations (7)-(18) of this paper predict the $T^{3/2}$ renormalization.

[13] F. Dyson, Phys. Rev. 102, 1217 (1956).

[14] S. Foner, Phys. Rev. 107, 68 (1957).

[15] F. M. Johnson and A. H. Nethercot, Jr., Phys. Rev. 114, 705 (1959).

LOW-TEMPERATURE THERMAL CONDUCTIVITY OF POLYETHYLENE

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The thermal conductivity of a sample of polyethylene has been measured in the temperature range below 1°K. The results obtained are inconsistent with previous theories offered to explain thermal conduction in these materials at higher temperatures; a simple modification to the theory is suggested which is consistent with the current data.

The thermal conductivity of polyethylene has been measured in the temperature range 1-4.5°K by several investigators.[1,2] Their data indicate that the thermal conductivity in this temperature range can be fitted by an expression used by Chang and Jones in their analysis of the low-temperature thermal conductivity of glasses.[3] Thermal conductivity measurements have been made on a sample of polyethylene in the range 0.5-1.4 °K and our results below 1°K deviate from the Chang and Jones expression, having a lower power dependence on temperature than would be expected from this expression.

The measurements were made on a commercial sample of polyethylene of density 0.947 g/cm^3 or fractional crystallinity about 65%. A standard He^3 cryostat and sample arrangement were used in making the measurements. The sample was in the form of a cylinder of length 3 cm and diameter 1 cm. The top of the sample was attached to a threaded copper post on the bottom of the He^3 chamber, and a heater was wound directly onto the bottom of the sample. Allen-Bradley $\frac{1}{8}$-W resistors of nominal resistance 10 Ω were used as secondary thermometers and were inserted into small holes drilled through the sample at spacings of about 0.8 and 0.5 cm, respectively, for two different experimental runs. These thermometers were calibrated directly against the vapor pressure of liquid He^3. Figure 1 shows the results of measurements made in the two different runs with the above sample. Because of the consistency of the results between the two runs, it is assumed that the relatively small thermometer spacing had little effect on the observed temperature gradients in the sample.

The Chang and Jones expression for thermal conductivity is obtained by assuming, as suggested by Klemens,[4] that only longitudinal phonons contribute to the low-temperature thermal conductivity, and that the mean free path due to structure scattering is $(A/a)k^{-2}$, where k is the

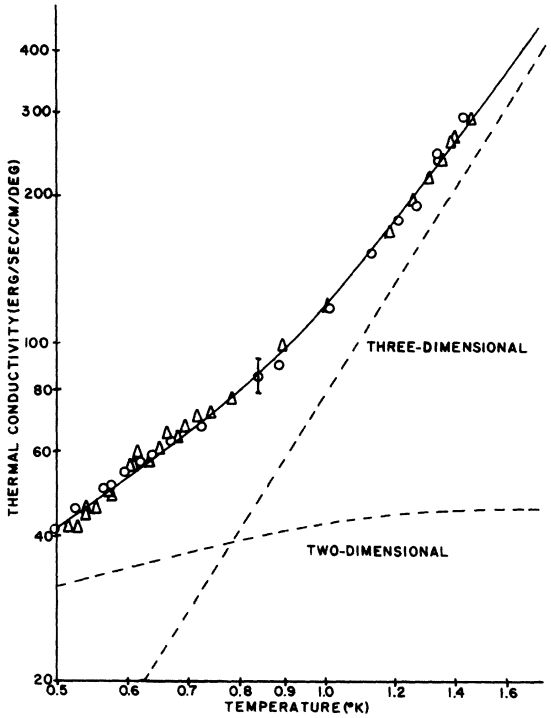

FIG. 1. Thermal conductivity of 65% crystalline polyethylene versus temperature. The open circles and triangles represent the results of two runs on the same sample. The solid curve represents the fit of Eq. (2) to the data using parameters given in the text and the dashed lines represent the separate contributions to κ as given by Eq. (2).

phonon wave vector and A/a is a parameter with the dimensions of reciprocal length. A constant mean free path l_2 due to scattering from internal boundaries is also included, and a Debye ω^2 frequency distribution is used, yielding the result

$$\kappa=\frac{K^2T}{6\pi^2\hbar}\frac{A}{a}\int_0^\infty\frac{x^4e^x}{(e^x-1)^2}\frac{dx}{x^2+(A/l_2)(\hbar v_1/KT)^2}, \tag{1}$$

where v_1 is the sound velocity of longitudinal waves and K is Boltzmann's constant; values of the integral in (1) have been tabulated by Callaway.[5]

To fit our data below 1°K, we suggest that Eq. (1) may be modified by the addition of a term to account for a mode of vibration mentioned by Wada[6] and observed by Barker[7] in the measurement of Grüneisen numbers in polyethylene: At sufficiently low temperatures, the dominant vibration process in polyethylene may be vibrations between polymer chains, the chains themselves remaining relatively rigid. Viewing these low-temperature vibrators as a two-dimensional array of rigid rods and using a two-dimensional frequency distribution proportional to ω, together with the same scattering processes used by Chang and Jones, we obtain the following modified expression for the low-temperature thermal conductivity of chain polymers:

$$\kappa=\frac{K^2T}{6\pi^2\hbar}\frac{A}{a}\int_0^\infty\frac{x^4e^x}{(e^x-1)^2}\frac{dx}{s^2+(A/al_2)(\hbar v_1/KT)^2}+\frac{CKv_2}{4\pi}\frac{B}{b}\int_0^\infty\frac{x^3e^x}{(e^x-1)^2}\frac{dx}{x^2+(B/bl_2)(\hbar v_2/KT)^2}, \tag{2}$$

where the first term is due to three-dimensional vibrations and the second term due to two-dimensional vibrations. The same value of l_2 is assumed for both two- and three-dimensional vibrations. $(B/b)k^{-2}$ is the structure scattering mean free path for the two-dimensional vibrations, v_2 is the phonon velocity associated with the two-dimensional vibrations, and C is a parameter with the dimensions of reciprocal length which may be related to the number of planar-lamellar vibrating systems per unit sample thickness.

Figure 1 shows a fit of Eq. (2) to our data and also shows the individual contributions to the thermal conductivity from the two- and three-dimensional vibrations. The parameters used for the fit were such that $A/a = 1.04\times10^{10}$ cm^{-1}, $v_1 = 2.31\times10^5$ cm/sec, $(B/b)v_2^2 = 1.38\times10^{17}$ cm sec^{-2}, $l_2 = 3.2\times10^{-5}$ cm, and $C = 1.39\times10^6$ cm^{-1}. In this temperature range, the first term in Eq. (2) is extremely insensitive to choice of the parameter A/al_2, hence it is difficult to attach definite meaning to the parameters at this time. Forthcoming measurements at higher and lower temperatures will be required for an accurate determination of these parameters as well as for a check on the T^2 temperature dependence predicted in the low-temperature limit by the modified expressions of Eq. (2). Measurements made on partially crystalline nylon and Teflon[8] gave little indication of the above observed behavior in the temperature range investigated; however, since the two-dimensional vibrations are strongly dependent on the nature of the forces between polymer chains it is not reasonable to expect all partially crystalline polymers to exhibit this behavior under the same conditions.

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[1] W. Reese and J. E. Tucker, J. Chem. Phys. 43, 105 (1965).

[2] R. J. Kolouch and R. G. Brown, J. Appl. Phys. 39, 3999 (1968).

[3] G. K. Chang and R. E. Jones, Phys. Rev. 126, 2055 (1962).

[4] P. G. Klemens, Proc. Roy. Soc. (London), Ser. A 208, 108 (1951).

[5] J. Callaway, Phys. Rev. 122, 787 (1961).

[6] Y. Wada, in Proceedings of the Conference on Relaxation Phenomena in Polymeric Systems, Tokyo, Japan, September, 1966 (to be published).

[7] R. E. Barker, Jr., J. Appl. Phys. 38, 4234 (1967).

[8] A. C. Anderson, W. Reese, and J. C. Wheatley, Rev. Sci. Instr. 34, 1386 (1963).