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Experimental determination of the thermal conductivity of a conducting polymer: Pure and heavily doped polyacetylene

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Room-temperature values of the thermal conductivity (κ) of pure and heavily doped polyacetylene, both *cis* and *trans* isomers, have been experimentally determined using a new experimental approach for the determination of κ along the plane of the sample. We find that effects of radiation losses are substantial and take them into account in our analysis. For heat transport along the plane of the film, we find $\kappa=2.1$ mW/cm K for *cis*-$(\mathrm{CH})_x$ increasing to 3.8 mW/cm K after isomerization to *trans*-$(\mathrm{CH})_x$. After doping to the metallic regime, κ increases to 6.9 mW/cm K. The large increase in κ upon isomerization is associated apparently with the difference in the lattice heat conduction in these isomers. From the increase of κ after doping to the metallic regime, the free-carrier contribution is obtained. Using the Wiedemann-Franz ratio, we infer that the intrinsic electrical conductivity in metallic doped $(\mathrm{CH})_x$ is high and that the measured values are limited by the polymer morphology.

I. INTRODUCTION

Thermal conductivity, which is an important transport property in its own right, is sometimes a crucial experimental parameter in characterizing the fundamental electrical transport mechanism in metals.[1] The transport properties of polyacetylene have been investigated extensively in the last few years.[2] Three regimes of doping concentration y have been identified where the transport properties are distinctly different. In the dilute doping regime ($y<0.002$), a novel mechanism for the electrical conductivity has been suggested by Kivelson.[3] In this model, charge is carried by phonon-assisted electron hopping between soliton midgap bound states as the dominant mechanism. The pressure and temperature dependence[4] and the frequency dependence of the conductivity,[5] as well as the thermopower,[6] are in excellent qualitative agreement with that model. Alternatively, attempts to explain the results in terms of the variable range hopping predicted conductivity values which are off by 15 orders of magnitude and pressure and frequency dependences which are not consistent with the experimental results.

In the heavily doped regime, $y>0.07$, doped polyacetylene is metallic. The Pauli susceptibility,[7] linear term in the heat capacity,[8] and linear temperature dependence of the thermopower,[6] all imply metallic behavior with density of states at the Fermi energy, $N(\epsilon_F)\cong 0.1$ states/eV C atom. Optical absorption and electron energy-loss experiments suggested that the energy gap of pure $(\mathrm{CH})_x$ has closed (or at least reduced to a value less than a few tenths of an electron volt).

The intermediate regime $0.002<y<0.07$ is particularly interesting. The thermopower data in conjunction with the electrical conductivity data imply a sharp transition in the transport behavior at a concentration of about 0.002. The electrical conductivity reaches a high level $\sigma\sim 10$—$100\ \Omega^{-1}\,\mathrm{cm}^{-1}$, and the thermopower reduces at this concentration to metallic values. However, the Pauli susceptibility (and hence the density of states) remains small,[9] growing abruptly at concentrations in excess of $y\cong 0.05$ to values typical of the metallic state.

Thus, the above studies appear to imply the existence of three distinct concentration regimes separated by two relatively sharp transitions in the transport and magnetic properties.

In this paper, we describe our initial results for the room-temperature values of the thermal conductivity of $(\mathrm{CH})_x$ in the two extreme doping concentrations: pure and heavily doped *trans*-$(\mathrm{CH})_x$. We have found that measurements of this kind present severe experimental problems due to the relatively high radiation losses of the samples, typically thin free-standing films with thicknesses of about 100 μm. The radiation losses in a typical sample amount to values greater than the heat conducted through the sample. Thus, the conventional simple experimental method for determination of κ along the film direction, based on the assumption that the temperature gradient along the heat-conduction path is constant, is not applicable in this case. Moreover, due to the extremely-small-cross-section sample and its low thermal conductivity, a large portion of the heat losses are due to radiation from the heating element used for establishing the thermal gradient along the sample. This causes an additional source of error in measuring the heat flow through the sample in the conventional configuration.

We have developed and successfully employed a new experimental approach for measuring the thermal conductivity κ along the plane of the film. The results for κ obtained by us differ markedly from those published previously by four other groups of investigators.[10–13] In Sec.

II we describe in detail our experimental approach and analyze the major difficulties in achieving the correct experimental results.

Since polyacetylene can show a large apparent anisotropy in electrical conductivity resulting from an inhomogeneous doping concentration, and since a large anisotropy in the thermal conductivity of $(CH)_x$ has been claimed by Newman *et al.*,[12] we have measured the thermal conductivity perpendicular to the plane of the film, $\kappa_\perp$, as well. The results obtained for κ (along the plane of the film) and $\kappa_\perp$ are presented, discussed, and compared to previous results in Sec. III. The conclusions are summarized in Sec. IV.

II. EXPERIMENTAL TECHNIQUE FOR MEASURING κ

A. Measuring method

The most often employed method of measuring κ in the temperature range between room temperature and the low-temperature region is depicted schematically in Fig. 1(a). In this configuration, a temperature gradient is established along the sample and the temperature difference, ΔT, is measured over a portion of it. From the measured supplied heat flow P and ΔT, the thermal conductivity is readily obtained:

$$\kappa = \frac{P}{\Delta T}\frac{L}{A} , \tag{1}$$

where L is the length over which ΔT is measured, and A is the cross-sectional area of the sample.[14]

The underlying assumptions here are that the temperature gradient is a constant along the heat-conduction path, and that the heat flux is constant through the sample. The equivalent electrical circuit for the above configuration is that of an Ohmic conductor [Fig. 1(a)].

However, when the radiation from the sample is significant, especially in samples such as $(CH)_x$ where the heat conducted through the sample and the radiation losses are comparable in magnitude, both of the above assumptions do not hold and Eq. (1) is not applicable. The equivalent electrical circuit is that of a transmission line depicted in Fig. 1(b) where the horizontal resistors r represent the incremental resistance of the sample to the heat flow, and the vertical components g specify the incremental radiation losses. We will show that the temperature variation along the sample decays exponentially under these conditions, so that Eq. (1) is not valid. In our measuring method, we actually measure the heat flows at both ends of the sample and indeed find that they differ significantly. These values in conjunction with the following analysis allow us to obtain the true thermal conductivity.

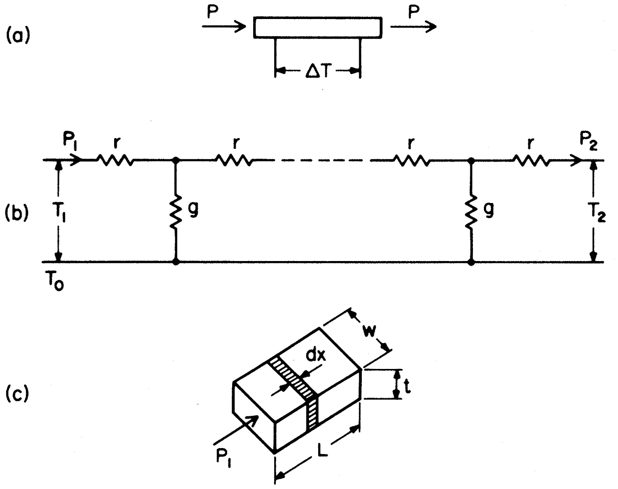

FIG. 1. (a) The most employed method of measuring the thermal conductivity where radiation heat losses are negligible. (b) Equivalent electrical circuit of a heat conductor with radiation heat losses. (c) Dimensions of a rectangular sample for which the heat equation is derived in the text.

For a rectangularly shaped sample, characterized by thermal conductivity κ and average emissivity $\bar{\epsilon}$, the solution of the heat equation is given in terms of the four boundary values: T_1,P_1 and T_2,P_2, which represent the temperatures and heat flows at the ends of the sample. T_0 is the ambient reference temperature and is absolute. All other temperatures are differences measured relative to T_0.

Assuming the dimensions of the sample to be L, w, and t, as shown in Fig. 1(c), and $t \ll L,w$, we have a one-dimensional heat-flow problem. The sample thermal resistance r per unit length is given by

$$r = 1/\kappa w t .$$

The radiation loss per unit length of surface [hatched area in Fig. 1(c)] is expressed by

$$g = 8(w+t)\bar{\epsilon}\sigma T_0^3 , \tag{2}$$

where σ is the Stefan-Boltzmann constant. The quantity g is the product of the sample periphery normal to the heat flow $2(w+t)$ and the derivative of the radiation law, $\bar{\epsilon}\sigma T_0^4$. In using the derivative for the radiation loss, we have assumed that the relative temperature differences are small. For all our measurements, T/T_0 was less than 1%.

If P represents the heat flow through the sample, we get the following equations (steady-state conditions are assumed):

$$\frac{dT}{dx} = rP, \quad \frac{dP}{dx} = gT .$$

The resulting heat equation is

$$\frac{d^2T}{dx^2} = rgT \equiv \alpha^2 T .$$

Substituting an assumed general solution

$$T(x) = Ae^{\alpha x} + Be^{-\alpha x} ,$$

we obtain

$$\frac{dT}{dx} = \alpha(Ae^{\alpha x} - Be^{-\alpha x})$$

and

$$P = \frac{1}{\beta}(Ae^{\alpha x} - Be^{-\alpha x}) , \tag{3}$$

where

$$\beta^2 \equiv r/g . \tag{4}$$

TABLE I. List of typical values of the dimensions of the samples and the temperatures and heat flows at the boundaries which were used in measuring the thermal conductivity. The temperatures T_1 and T_2 are measured relative to the ambient T_0.

$L=3.0$ mm	$T_1=1.00$ K
$w=7.0$ mm	$T_2=8.7$ mK
$t=89$ μm	$P_1=63$ μW
$T_0=302$ K	$P_2=45$ μW

Introducing the boundary values T_1,P_1, and T_2,P_2 at $x=0$ and L, respectively, we find

$$\alpha=(rg)^{1/2}=\frac{1}{L}\ln\left[\frac{T_2+\beta P_2}{T_1+\beta P_1}\right], \tag{5}$$

$$\beta^2=\frac{r}{g}=\frac{T_1^2-T_2^2}{P_1^2-P_2^2}. \tag{6}$$

Thus, by measuring T_1, T_2, P_1, and P_2, we find α and β and hence κ and $\bar{\epsilon}$. In Table I, we list typical values of the dimensions [defined in Fig. 1(c)], temperatures, and heat flows used at the boundaries of a test sample of polyethylene $(CH_2)_x$. This sample was used to verify the correct operation of the entire system. Note that even for the short sample we have used ($L=0.3$ cm), P_1 and P_2 are different. With more typical sample dimensions (larger L) used by other investigators, the ratio of P_1 to P_2 is expected to be much larger because of the exponential decay with length (a typical value of α is $-3\ \mathrm{cm}^{-1}$).

B. Apparatus for measuring κ

A schematic diagram of the apparatus that has been specially built for measuring the thermal conductivity along the film, κ, appears in Fig. 2. The ends of the sample are tightly clamped in the copper clamps, C_1 and C_2, so that a good thermal contact is established between sample and clamps. A large copper shield S is located in the middle of the apparatus perpendicular to the sample. The sample is placed through a narrow slot in the shield without touching it. This shield eliminates nearly all direct radiation heat exchange between the sample clamps. A third dummy clamp C_3 (also of copper) is located beside C_2. Clamp C_3 is shown below C_2 for clarity but it is the same height as C_2 for best compensation as mentioned below.

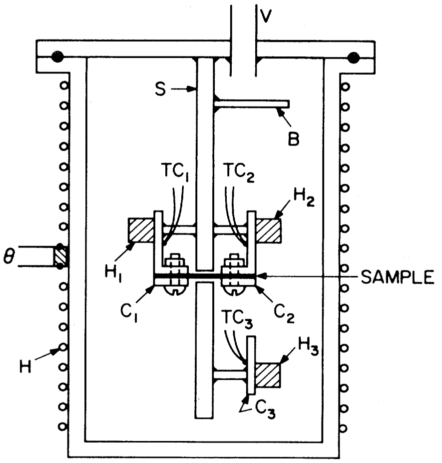

FIG. 2. Schematic diagram of the apparatus for measuring the thermal conductivity.

All clamps are weakly thermally connected to the shield by stainless-steel supports. The clamp temperatures are monitored by three separate differential thermocouples (TC_i) with their references thermally connected to the shield. The thermocouples are of Chromel-Constantan which provides maximum output voltage, and because of its low thermal conductivity is readily thermally anchored. Thermocouples are thermally anchored on the clamps in the following way. They are soldered to relatively wide strips of copper foil which are glued onto the copper clamps using GE 7031 varnish with thin sheets of glass interposed for electrical insulation. Each of these clamps can be heated individually by a small Manganin heating element H_i attached to it. These heaters were wound in a single layer to minimize radiation losses and situated such that no radiation from them could directly reach the active part of the sample. The upper end of the shield is attached to the inner side of the flange of the copper vacuum can, where a high vacuum is maintained during the measurement ($\sim 5\times 10^{-6}$ Torr). The vacuum pumping line V is made of stainless steel to minimize the heat leak and avoid a large concentrated leak. The baffle B is to shield the clamps from direct radiation from V. The temperature of the outer can is regulated at T_0 by means of a thermistor θ and heater H attached to it, which are connected to an electronic controller. We have found that small fluctuations in the temperature of the outer can cause significant fluctuations in the measured temperature of all the clamps. In order to reduce the effect of these fluctuations, the temperature increases of C_1 and C_2 are evaluated with respect to that of the dummy clamp C_3. The three clamps were constructed to have similar response times in order for this procedure to be effective.

C. Experimental procedure

The temperature distribution for a given ambient temperature T_0 is set up by creating a temperature gradient along the sample and, hence, producing a heat flux through it. The remaining two parameters required for obtaining κ and $\bar{\epsilon}$ are the heat flow at two ends of the sample P_1 and P_2 [see Fig. 1(b)]. These heat flows are obtained in a less direct way than T_1 and T_2. Their values at either C_1 or C_2 are deduced by the temperature of each clamp owing to the direct relation between T_i and the power injected at the clamp in a steady-state condition. To elucidate this procedure, we show the equivalent diagram of the actual apparatus in Fig. 3.

G_1 and G_2 represent the total thermal conductance of the clamps, which are mostly conduction through the supports of the clamps (to the shield) and radiation. The heat path in Fig. 3 includes the heat conducted through the sample and the radiation energy exchanged between C_1 and C_2 through the slot in the shield. In Fig. 3 we omit

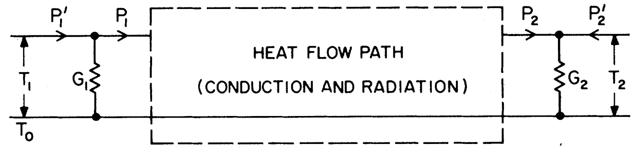

FIG. 3. Equivalent electrical diagram of the measuring apparatus in a steady-state condition.

the parameters which are related to the heat capacity of the different components of the apparatus. They only determine the response time and are unimportant to the relations which we seek for the evaluation of κ and $\bar{\epsilon}$. (We do, however, take sufficient time for the measurements to find the equilibrium values.)

On the left-hand side of the diagram in Fig. 3, P_1' represents the total electrical power supplied by heater 1, and P_1 is the portion of this power that is injected into the sample plus that radiated from side 1 to side 2 through the small slot in the shield. Similarly, P_2' and P_2 represent the total power injected and the power which comes out of the sample plus that radiated, respectively, on the right-hand side.

We define the following conductances:

$$G_1=\frac{P_1'-P_1}{T_1}\,, \tag{7}$$

$$G_2=\frac{P_2'+P_2}{T_2}\,, \tag{8}$$

$$G_{12}=G_2\left.\frac{T_2}{T_1}\right|_{P_2'=0,\;P_1'>0}=\frac{P_2}{T_1}\,, \tag{9}$$

where, as before, T_1 and T_2 are measured relative to T_0.

Two measuring runs are performed at each ambient temperature T_0. The first one is without a sample and the second one is with it. In the former measurement, the values of G_1, G_2, and G_{12} are determined, basically by applying a measured injected electrical power at each clamp separately and recording the resulting increase in temperature at both clamps, C_1 and C_2. Then, in the latter run with a sample in, only side 1 is heated and from the resulting changes in temperature T_1 and T_2 we find G_1 and G_{12}. The effective changes in the conductances G_1 and G_{12} due solely to the sample are obtained by subtraction of the conductances which were found in the former run (without a sample) from the latter obtained conductances. Finally, from the changes of G_1 and G_{12} and the measured T_1, we obtain the required net injected heat into the sample P_1, and the heat conducted out of it, P_2, while eliminating the effect of the radiation through the slot. In fact, the values of the conductances, G_1 and G_{12}, which are used for obtaining P_1 and P_2 are average values of those measured in each of the above runs in a cumulative sequence of a few heating and cooling steps. This procedure eliminates the effects of small extraneous heat inputs or offsets in the thermocouple outputs. It should be emphasized that it is important for the temperatures of the can and shield to be uniform and at the assumed T_0. From Figs. 1(b) and 3, all heat leaks terminate at T_0, and the usefulness of the analysis depends on this being true.

Another assumption made in this analysis is that the exchange of radiation between the sample clamps, C_1 and C_2, through the slot in the shield is not affected in a significant way by the presence or absence of the sample in the apparatus in the two measuring runs. This is a valid assumption due to the very small size of the slot and, hence, the small amount of radiation leaking through it compared to the heat flow through the sample. This is demonstrated in Table II where P_1 and P_2 are much smaller in line (A) than in line (B).

So far we have assumed that all lateral heat exchange between sample and environment is governed by blackbody emission of the environment at temperature T_0. The sample is surrounded in our probe mostly by copper, and if its reflectivity were high the apparent conductivity of the sample could be increased due to radiation emitted by the hotter part of the sample being reflected by the environment and reabsorbed at the cooler part of the sample. The copper parts in our probe were allowed to develop a natural oxide coating and therefore have a moderate emissivity. In particular, the slot in the middle of the shield is rough and thus scatters radiation diffusely. We have estimated the effects of the above radiation coupling in our system to be small. The effective sample length L used in the analysis is the free length between the clamps C_1 and C_2 in Fig. 2, and is obviously much less than the overall length of the sample. In each sample clamp the lower jaw is joined thermally to the upper one by copper-foil straps, and thus heat is coupled in or out of both surfaces of the sample. After removal from the apparatus, the samples were observed to have impressions of the clamps, validating the good thermal contact. Small additional heat losses due to the imperfect vacuum are absorbed into g and result in a larger effective value of $\bar{\epsilon}$, which is of no immediate interest in the analysis.

There is one small correction to the final values of κ which has not been mentioned yet. In Table I the sample thickness t is not completely negligible compared to the length L as assumed in the analysis. This results in a sig-

TABLE II. Typical experimental values of the measured temperatures and heat flows at the two clamps of the apparatus C_1 and C_2 and at the boundaries of a measured $(CH_2)_x$ sample. Note that T_1 and P_1' must be measured with high fractional resolution.

Run	T_1 (K)	T_2 (mK)	P_1' (μW)	P_1 (μW)	P_2 (μW)
(A) Without sample	1.0000	2.3	4952	12	12
(B) With sample	1.0000	11.0	5015	75	57
(C) Difference (B)−(A)		8.7	63	63	45

TABLE III. Room-temperature results of κ for undoped *cis*- and *trans*-$(CH)_x$, heavily doped *trans*-$(CH)_x$, and polyethylene samples. The last column is for the sample detailed in Tables I and II.

	Cis-$(CH)_x$	*Trans*-$(CH)_x$	10% doped *trans*-$(CH)_x$ with AsF_5	Polyethylene
κ (mW/cm K)	2.1	3.8	6.9	2.5
$\bar{\epsilon}$	0.23	0.32	0.29	0.14
σ $(\Omega\,\mathrm{cm})^{-1}$			270	
κ_e (mW/cm K)			1.9	

nificant nonuniform temperature gradient only where the sample enters the clamps. An analog model of the geometry was set up using conducting paper to estimate the correction which was computed for each sample presented in Table III. The average correction was approximately $+4\%$ for κ.

Typical experimental values for the sample used in obtaining Table I are listed in Table II. Note that the sample is a small perturbation of P_1'. This means G_1 in Fig. 3 must be extremely stable through disassembly of the apparatus and sample mounting if measured changes in the value P_1 are to be meaningful. The supports for the clamps are made in the form of a cage of stainless-steel wires joined by hard solder to brass end plates. This construction of the support gives a very rigid mounting (for a stable radiation leak) and good thermal contact at its ends (for a stable conduction leak).

III. RESULTS AND DISCUSSION

A. Present results of the thermal conductivity of $(CH)_x$

The room-temperature results of the thermal conductivity κ along the plane of the film for undoped *cis*-$(CH)_x$, and undoped *trans*-$(CH)_x$, as well as doped *trans*-$(CH)_x$, are summarized in Table III. The samples were prepared by the method of Ito *et al.*[15] and were mounted in the apparatus under a hood of flowing argon. We include the results for κ for a commerically produced thin sheet of polyethylene. This was measured in order to check our newly made apparatus. The degree of crystallinity of this polyethylene sample was estimated by x-ray studies to be 33%. Considering the uncertainty in the x-ray measurements, the results are in good agreement with the expected value.[16]

In order to evaluate the accuracy of our measurements, we have made several additional tests. The results for polyethylene in Table III are the average of two measurements made one month apart, with several other samples having been measured in the interim. The individual measurements of κ for polyethylene differed by 4% from the value in the table which is an indication of the reproducibility of the method (random error). This sample actually consisted of two sheets (stacked so as to double the thickness) so that the conductance G_{12}, although lower, was comparable to that existing when $(CH)_x$ samples were measured. To check whether the samples were in the optimum measuring range of the apparatus, we tested it with known samples having lower and higher thermal conductances. For the low end, a single sheet of the polyethylene was run and yielded a result for κ that agreed with that for the two sheets to within the accuracy of the apparatus. Examining Table II again, we see that for a single sheet the heat conducted through the sample and that radiated through the slot will now be comparable, and yet reasonable results are still obtained. This behavior demonstrates that poorly conducting samples do indeed yield accurate values of κ. For the high end, the situation is more difficult. We are not aware of a material having a somewhat higher conductivity which is also sufficiently soft (in order that the clamps make adequate thermal contact). As an approximation, we ran a very thin sheet of stainless steel. This has a thermal conductivity more than 20 times the highest value listed in Table III, which even when combined with its thinness would be expected to have a conductance exceeding that of any of the measured samples. In fact, the measured value was the highest ever seen in our apparatus, although it was lower than predicted. Considering that stainless steel is harder than the copper clamps (the polymers are much softer) and the piece tested was thinner than any sample, it is not surprising that the thermal contact was inadequate. However, this check demonstrates that if polyacetylene did have the high value of thermal conductivity claimed by the other investigators, it would certainly have indicated so in our measurements, even if the accuracy were slightly reduced. After estimating the uncertainties in the various quantities contributing to a measurement (see Table I), we conclude that our overall uncertainty for κ is 20%, where about one-half of it is systematic error.

The first interesting feature exhibited in Table III is the large increase in the heat transport upon isomerization of the polymer from *cis*-$(CH)_x$ to *trans*-$(CH)_x$. The 75% increase in κ can be attributed to the following different origins: (a) the difference in the lattice contribution to κ of the two structurally different isomers, (b) the difference in the contribution of the radiation heat transfer, and (c) the contribution to the heat transport due to the topological domain-wall excitations, often referred to as solitons, which are created during the isomerization process.

The relative contribution of each of the above effects cannot easily be separated. This is, on one hand, because of the lack of experimentally viable information regarding the phonon dispersion relations in $(CH)_x$, and on the other hand, the difficulties attendant in quantitative theories of heat transport, by conduction and radiation mechanisms, in anisotropic materials. Thus, in view of that, all that we attempt here is to construct a scale of magnitude of contributions to κ of the above effects.

Starting from the third effect we can envision a rather high contribution to κ from each of the highly mobile neutral solitons because of its small effective mass and its high diffusivity along the chain direction.[17,18] Here it is this parallel diffusivity that may govern the heat conduction in contrast to the perpendicular interchain diffusion rate which is smaller by six orders of magnitude,[17] and which sets the limit for the electrical conductivity via the intersoliton electron hopping mechanism. The contribution to κ from the diffusing solitons driven by the gradient in the density of the phonons along the sample is similar, to some extent, to the effect of thermophoresis. Although each soliton may be quite efficient in heat conduction the total contribution of these defects to κ is only a fraction of a percent of the increase in κ upon isomerization. This is due to their low density in undoped *trans*-$(\mathrm{CH})_x$.

The second relevant heat-transport mechanism is the radiative heat transfer κ_r. Assuming that kinetic theory arguments are applicable to a gas of photons, κ_r in inhomogeneous materials is governed by the photon mean-free path. The photons are scattered by the irregularities in the refractive index due to the fibrils and the voids in the free-standing film of polyacetylene. The mean-free path $l(\nu)$ may vary as $1/\nu^4$ for the lowest frequencies, when these irregularities are small compared to the wavelength (Rayleigh scattering) and may even reach the sample dimensions. Klemens and Greenberg[19] have discussed the radiative heat transfer in random assemblies of fibers and obtained $\kappa_r = 4\sigma n^2 L T^3$, where σ is the Stefan-Boltzmann constant, n is the refractive index, and L is the order of the shortest linear dimension of the specimen. Applying this formula, we find $\kappa_r \sim 10^{-4}$ W cm^{-1}K^{-1} at 300 K, which is one order of magnitude less than the change of the thermal conductivity upon isomerization.

The above estimates then lead us to conclude, by way of elimination, that the dominant cause of the change in κ between *cis*- and *trans*-$(\mathrm{CH})_x$ must be due to the difference in the lattice heat conduction of these two isomers.

From the values of the room-temperature sound velocity v of *trans*-$(\mathrm{CH})_x$ and specific heat c_V, measured by Guckelsberger *et al.*,[11] as well as the value of the heat conductivity in Table III, we have calculated the phonon mean-free path $l = 3\kappa / c_V v$ to be approximately 12 Å at 300 K. This value can be viewed as the lower limit for the mean-free path due to the morphology of the fibrillar polyacetylene free-standing films, which may limit the measured value of κ and thus the derived mean-free path.

A second interesting feature presented in Table III is the significant increase of thermal conductivity after doping to the metallic regime from 3.8 to 6.9 mW/cm K. This implies a large electronic contribution. Using the measured value of the electrical conductivity, σ, we find the increase in κ due to the doping is 62% greater than expected from the Wiedemann-Franz ratio alone (κ_e in Table III). Considering the further degradation of the degree of crystallinity after doping the film due to the random location of the dopant molecules, and hence the increase number scattering centers, we can assume that the ultimate intrinsic possible electrical as well as thermal conductivities in an ordered doped polymer would be much higher.

In polyacetylene films with their fibrillar morphology, the apparent conductivities are dependent on the intrinsic intrafibril conductivities as well as on the nature of the barriers at the interfibril contacts. Assuming the Wiedemann-Franz law holds at high doping levels at room temperature, we find that the intrinsic intrafibril electrical conductivity σ_{WF} of the fibril is greater than the apparent conductivity σ. As was suggested by Mermilliod, Zuppiroli, and Francois[10] high potentials at the interfibril contacts may stop the charge carriers, but the phonons can act as thermal short circuits. The thermal conductivity is, therefore, less sensitive to the lattice defects than is the electrical conductivity. This interpretation agrees with several other experimental results on highly doped samples that suggest large differences between the intrinsic and the apparent conductivities.

We note that our results summarized in Table III were derived from the experimentally obtained conductances of the various samples normalized to their external dimensions. No attempt was made to take into account either the fibrillar structure of the films in deriving the thermal conductivities or any changes in the dimensions of the fibrils themselves upon isomerization or doping. However, the sample dimensions were measured just before mounting in the apparatus (isomerization or doping were done separately) so that if the external dimensions changed with treatment, this was taken into account, i.e., the current dimensions were used.

B. Comparison and analysis of previous results of κ of $(\mathrm{CH})_x$

Our results are markedly different from those obtained by four other groups of investigators.[10–13] The common feature of their results are the relatively high values of the thermal conductivity κ along the plane of the film (from 20 to 250 times ours) and the strong (increasing) temperature dependence of κ for temperatures above approximately 100 K. According to the analysis and arguments presented in Sec. II, the higher obtained values of κ are a result of employing an inapplicable measuring method where significantly high radiation losses were neglected. The strong temperature dependence of κ along the film direction found by these authors probably stems from the dominating extraneous radiation contribution that was not separated experimentally.

Owing to the rather large differences between our results and those of the previous investigators we attempt in the following to consider their measurements in detail.

To analyze the previous measurements semiquantitatively, we simplify our derivation to correspond to the conventional method. In Fig. 1(b) this means setting $T_2 = 0$, which is equivalent in Fig. 2 to mounting clamp 2 in good thermal contact with the shield S, i.e., the "cold" end of the sample is now at the reference temperature T_0. Such an arrangement, of course, precludes the measurement of P_2, which we have found crucial in obtaining an unambiguous result. One extreme situation is where the direct radiation from the heater (H_1) is negligible. In Fig. 3, this corresponds to setting $G_1 = 0$, in which case

P_1 is correctly measured as the heater input power. Setting $x=0$ (side 1) in Eq. (3) and using Eq. (4), we see that P varies as $g^{1/2}$. From Eq. (2), the overall dependence of P is then $T_0^{3/2}$, characteristic of a distributed radiator. Substituting P into Eq. (1), the result is κ also varying as $T^{3/2}$. (We have ignored the factor $r^{-1/2}$ which varies as $\kappa^{1/2}$, since the quantity typically has a weak temperature dependence, especially for disordered materials.) Examining the data for κ from the four published groups (they are all graphed together in Ref. 13), we find that for Refs. 10 and 12 the temperature dependence is close to $T^{3/2}$. In Ref. 10, the heater is just a fine wire wound directly on the sample and would be expected to have a small radiation loss because of its small surface area. In Ref. 12 (the apparatus is described in more detail in Ref. 20), the heater is inside a gold-plated block and the low emissivity of the gold should result in a low radiation loss. At the other extreme, the direct radiation from the heater dominates (as in our apparatus). In this case, G_1 is large and takes on the dependence of $g \sim T_0^3$, characteristic of a lumped radiator. The heater power is now P'_1, a very small amount of which even passes into the sample (and even less comes out the other end). Again, using Eq. (1), κ should now vary as T^3. In Ref. 11, the data for κ varies as T^3, a fact indicated explicitly on the original graph. Unfortunately, Ref. 11 gives no description of their apparatus; therefore, we cannot determine why the heater loss is so large. However, our analysis does make a further prediction. A dominant heater loss will make the value of P substituted into Eq. (1) even larger than the already excessive value for when the heater is lossless and should lead to an enormous result for κ. In fact, this is so: The value of κ at room temperature in Ref. 11 is nearly an order of magnitude higher than that reported in Refs. 10, 12, and 13, which in turn are about an order of magnitude higher than our values.[21] In Ref. 13, the dependence of κ is about T^2, which implies a heater loss comparable to the sample conduction. Again, there is no description of the apparatus in Ref. 13, so we cannot analyze it further.

So far, we have considered possible errors in the determination of the power P. The use of a differential thermocouple attached directly to the middle of the sample (as described in Ref. 10) may result in an incorrect temperature difference. ΔT. Even though alloy wires may be used, their thermal conductivity is much larger than that of the sample and would result in a value of ΔT which is too small. From Eq. (1) we see that such an error also leads to a higher value of κ. Also, gluing the thermocouple wires to the porous $(\mathrm{CH})_x$ sample (filling factor typical $\frac{1}{3}$) with organic glue with a comparable conductivity to $(\mathrm{CH})_x$ may result in additional error due to the spread of the glue into the sample.

Some of the previous authors[10] explicitly considered heat losses from radiation and the various wires in their final analysis, but because they used the simplified model of Fig. 1(a) and initially concluded that their sample had a high thermal conductivity, they judged the stray losses to be minor. However, a new material such as $(\mathrm{CH})_x$ must be assumed *a priori* to have unknown parameters. We have attempted to verify the range of satisfactory operation of our apparatus using known samples. (Those materials were originally measured using a large sample where the special problems associated with thin films are absent.) If the results for the $(\mathrm{CH})_x$ samples had fallen outside the demonstrated range of our apparatus, they would have been rejected.

Note that in Table III, $0<\bar{\epsilon}<1$, a necessary condition if our approach is correct. Also, we point out that if we had used our apparatus conventionally, i.e., in Table II we only used T_1 and P'_1 of run (B), we would have deduced a value of κ about *100 times as large* as the true one. This is in the middle of the range of values found by the previous four groups.

If the values for the effective $\bar{\epsilon}$ could be estimated for some of the previous measurements, the data could be corrected for radiation losses. This would be useful because our present apparatus can only be used near room temperature while the others have measured over a wide range. The correction of the previous data is especially important above about 100 K. Below 50 K the data of Refs. 10 and 11 is in agreement and would not be expected to be significantly affected by radiation losses.

Initial study of the thermal conductivity of undoped polyacetylene in a direction perpendicular to the plane of the film, $\kappa_\perp$ (using a different apparatus), yielded results which indicate that $\kappa_\perp$ is essentially the same as the one obtained along the film direction. We thus conclude that the thermal conductivity of undoped polyacetylene is practically isotropic in agreement with morphology of the fibrilous structure as revealed by scanning electron microscopy where random orientation of the fibrils is evident.

These findings are also in agreement with a recent study of the dependence of the electrical conductivites, $\sigma_{\parallel}$ and $\sigma_\perp$, on the degree of homogeneity of the doping[22] in *trans*-$(\mathrm{CH})_x$. For undoped films as well as for uniformly doped ones, the ratio of $\sigma_{\parallel}/\sigma_\perp$ is found to be about 2, which is interpreted to be solely due to small preferential orientation of the fibrils.

The large ratio of the in-plane thermal conductivity to $\kappa_\perp$ as obtained by Newman *et al.*[12] is inconsistent with the randomlike morphology of the fibrils in $(\mathrm{CH})_x$. Moreover, the marked difference in the temperature dependence of the above conductivities obtained by these authors may originate from the reduction of the relative radiation losses in the perpendicular measuring configuration. This is mostly because of the higher measured conductance in this direction due to the significant reduction in the length of the heat path and the large increase in cross section.

IV. CONCLUSIONS

We have developed a new method for measuring the thermal conductivity of thin and poorly conducting films and successfully applied it to undoped and heavily doped polyacetylene. A large increase in κ occurs upon isomerization as well as upon doping the sample. The first increase is concluded to be due to the difference in the lattice vibration contribution between *cis*- and *trans*-$(\mathrm{CH})_x$. The phonon mean-free path at room temperature is found to be approximately 12 Å. Radiative heat transfer and the contribution due the mobile neutral solitons are estimated to be less important.

After doping to the metallic regime, the obtained thermal conductivity indicates metallic behavior with intrinsic electrical conductivity greater than the apparent one limited mostly by interfibril contact barriers. A continued study of the thermal conductivity in the direction perpendicular to the film is in progress and will be published subsequently. Finally, it seems that the heat transport of polyacetylene at the two extreme *doping* regimes, undoped and heavily doped samples, is governed by single-carrier mechanisms. It would be quite interesting to further explore the thermal conductivity in the intermediate doping region where the transport might proceed as a result of collective motion in this regime where a high density of solitons is known to be present[22,23] and yet the measured Pauli susceptibility is very small.

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