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Thermoelectric power and conductivity of heterogeneous conducting polymers

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We discuss the interpretation of thermoelectric power in heterogeneous media, and using a compilation of many sets of data, we analyze the thermopower of conducting polymers as a function of conductivity and of temperature. For samples of very high conductivity, the thermopower (but not the conductivity) shows typical metallic temperature dependence, which is consistent with a heterogeneous model of metallic fibrils separated by thin electrical barriers. Metallic thermopower is expected rather generally to show significant nonlinearities as a function of temperature, and we demonstrate that the observed thermopower in some highly conducting polymers is very similar to the diffusion thermopower of metals in which a knee is produced at low temperatures by the electron-phonon interaction. The thermopower of moderately doped conducting polymers, like their conductivity, is generally consistent with a significant contribution from variable-range hopping.

I. INTRODUCTION

The development of polymers with high electrical conductivities[1-3] has led to considerable interest in the mechanism of conduction and the role played by hopping between localized states, solitons, disorder, tunneling, and inhomogeneities.[4] A frequently observed feature of the conductivity of lightly doped polymers is the similarity of its temperature dependence to the Mott law for variable-range hopping between localized states[5] (the states in the vicinity of the Fermi level may be solitonlike[6]). For heavily doped polymers, the conductivity attains values comparable to those in metals and can remain finite in the zero temperature limit, but its temperature dependence generally still has the *opposite* sign to that typical of metals (i.e., conductivity increases with temperature). The thermoelectric power, in contrast, often shows metallic size *and temperature dependence* for heavily doped samples.[7]

In this paper, we have compiled thermopower data for a large number of polymer samples.[6-18] We find a well-defined correlation between the magnitude of thermopower and conductivity for doped polyacetylene which is consistent with a major contribution from variable-range hopping for dopant concentrations up to a few percent. We also analyze the temperature dependence of thermopower with particular emphasis on the most metallic samples, for which we make a new suggestion that can account for observed nonlinearities.

It is true that highly disordered metals show a reversed temperature dependence of their conductivity (the Mooij correlation) ascribed to incipient localization,[19,20] while thermopower temperature dependence is not greatly affected.[21] However, it is doubtful that this mechanism is able to account for the observations on the very highly conducting polymers.[22] For example, an almost temperature-independent conductivity has been seen at helium temperatures,[11,10,23] rather than the anomaly characteristic of disordered materials. Further, the mean free path in the most highly conducting samples[24] is too long for incipient localization to have such a large effect (at least in a homogeneous model). As proposed by several authors,[11,10,5] heterogeneous models involving good metallic conduction in fibrils separated by thin barrier regions appear to be appropriate.

Previous treatments of the thermoelectric power of inhomogeneous polymers[25,26] have calculated the thermopower by substituting the total conductivity in the standard Mott formula

$$S=\frac{\pi^2k^2T}{3e}\frac{d\,\ln\sigma(E)}{dE}\bigg|_{E_F}\,, \tag{1}$$

where k is Boltzmann's constant, T temperature, e electronic charge, $\sigma(E)$ a conductivitylike function of electron energy E, and E_F is the Fermi energy. We point out here, however, that this procedure, which implies that the regions dominating resistance also dominate thermopower, is correct only for the particular special case in which thermal resistance is proportional to electrical resistance. We give a more general treatment of thermopower in a heterogeneous material, and show how the contribution made by different regions to the total thermopower can be weighted differently from their corresponding contributions to the total conductivity. In particular, we illustrate how thermopower can exhibit metallic temperature dependence while the conductivity is still limited by thermally assisted conduction.

Given the apparent importance of metallic conduction in some polymers, it is desirable to analyze data using the correct temperature dependence of metallic thermopower. It is something of a misconception that metallic thermopower is proportional to temperature in the absence of phonon drag—such behavior has almost never been observed.[27] The Mott formula is applicable for situations where conduction occurs in the vicinity of the Fermi level,[28] and the conductivity function $\sigma(E)$ is slowly varying in a region of width a few times kT about the

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Fermi level. It is therefore not able to account for the temperature dependence of the effect of the electron-phonon interaction on diffusion thermopower,[29] because this interaction causes electronic properties to vary on the scale of the Debye energy about the Fermi level. We give a detailed analysis of some highly conducting polymer thermopowers in terms of the metallic model that has been successful for glassy metals,[29] in which a characteristic nonlinearity of thermopower with temperature arises from enhancement at low temperatures by the electron-phonon interaction. This enhancement effect, which is analogous to the electron-phonon enhancement of specific heat, is a general effect in metallic diffusion thermopower,[30] but is masked by larger nonlinearities due to phonon drag in good crystalline metals.

II. THERMOPOWER AND CONDUCTIVITY IN HETEROGENEOUS MEDIA

In this section we give general expressions for the thermopower and conductivity of media such as fibrillar polymers composed of one type of material connected electrically by sections of a second type of material. Our principal purpose here is to show how the thermopower arising in each type of material must be combined to yield the total observed thermopower; specific models for each type of material are considered in the following section.

We consider a sample composed of two different types of material, with conductivities σ_1 and σ_2, in series in the conduction path, as in the particular example (Fig. 1) of a polymer with fibrils connected by barrier regions of different conductivity, or of fibrils with regions of different conductivity (multiple fibril connections should not change our main conclusions). Summing fibrillar paths j in parallel, the total conductivity of the sample is

$$\sigma = LA^{-1}\sum_j (L_{1j}A_{1j}^{-1}\sigma_1^{-1} + L_{2j}A_{2j}^{-1}\sigma_2^{-1})^{-1} , \qquad (2)$$

where L_{ij} is the total length of material of type i in the path j, A_{ij}^{-1} is the average inverse cross-sectional area of the fibril in region i, L is the length of the sample, and A its cross-sectional area. If the fibrillar conducting paths through the length of the sample all have the same fraction of their total resistance arising from regions of type 1, the total conductivity of the sample can be written in terms of the conductivities σ_i of the two different types of material with *temperature-independent* geometrical weighting factors f_i:

$$\sigma^{-1} = f_1\sigma_1^{-1} + f_2\sigma_2^{-1} . \qquad (3)$$

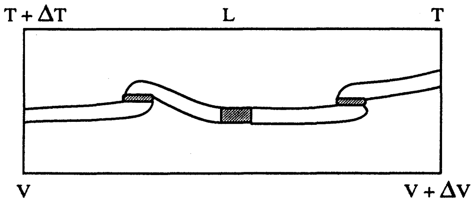

FIG. 1. Fibrillar conducting path through a polymer, consisting of regions of two types of material (open and shaded) in series. ΔV is the voltage between the ends of the sample produced by a temperature difference of ΔT.

For the case where all fibrillar paths have the same total resistance

$$f_i = L_i A/(LpA_i) , \qquad (4)$$

where p is the number of fibrils passing through the cross-sectional area. Note that in general $\sum_i L_i$ will exceed L since the fibrils will not be aligned, and pA_i will be less than A, since the fibrils will not fill the entire volume of the sample and will not all be perpendicular to the sample cross-sectional area; both effects lower the conductivity. If the fibrils have different ratios of $L_1A_1^{-1}$ and $L_2A_2^{-1}$, and the conductivities σ_1 and σ_2 have different temperature dependences, the coefficients f_i will in general show some temperature dependence since the distribution of current between the fibrillar paths will vary with temperature.

If $\sigma_1 \gg \sigma_2$, (3) and (4) give

$$\sigma \approx (LpA_2/L_2A)\sigma_2 . \qquad (5)$$

Thus if the barriers are thin ($L_2 \ll L$) the total conductivity may be much larger than that in the barrier regions, but still have the same nonmetallic temperature dependence as the barrier conductivity σ_2. (If conduction through the barrier regions is by tunneling, σ_2 will not be their intrinsic conductivity, but similar reasoning will apply.) In a similar fashion, Greig and Sahota[31] found that the thermal conductivity in some polymers has a temperature dependence characteristic of the amorphous state but has a magnitude larger than that expected for an amorphous sample.

The thermoelectric power arising from the fibrillar path in Fig. 1 is

$$S = \Delta V/\Delta T = (\Delta V_1 + \Delta V_2)/\Delta T , \qquad (6)$$

where ΔV_i is the voltage drop across region i. If the fibrillar paths all have the same ratio of temperature drops ΔT_1 and ΔT_2 across material of type 1 and 2, respectively, the total thermopower of the sample, which is the average of the individual path thermopowers weighted by their contribution to conductivity,[32] is also given by (6). Since thermopower is an intrinsic quantity, the geometric factors in the conductivity expression are absent. The general expression for the thermopower for two types of material in series is then

$$S = (\Delta T_1/\Delta T)S_1 + (\Delta T_2/\Delta T)S_2 , \qquad (7)$$

where $S_i = \Delta V_i/\Delta T_i$ is the characteristic thermopower for each type of material. Thus the total thermopower is weighted in favor of the regions where the largest temperature gradient occurs, and the weighting of the different regions can vary markedly for different cases.

(i) Uniform temperature gradient. If the temperature gradient is uniform down the sample, and conduction through the "barrier" regions is perpendicular to the temperature gradient, as for the first and last barrier regions in Fig. 1, the total thermopower will be simply the thermopower of region 1, since $\Delta T_2 = 0$:

$$S = S_1 \; . \tag{8a}$$

In this case, the thermopower is determined entirely by the fibrils, with no contribution from the barriers even if they make the major contribution to resistance. Clearly this situation provides a mechanism for thermopower to show metallic behavior and for conductivity to be near metallic magnitude but show nonmetallic temperature dependence as in (5).

(ii) Heat current flows through the same fibrillar paths as electrical current. In this more realistic case, the temperature drop across each region is proportional to its thermal resistance W_i, so

$$S = (W_1/W)S_1 + (W_2/W)S_2 \; , \tag{8b}$$

where W is the total thermal resistance. We can still have $S \approx S_1$ but $\sigma \propto \sigma_2$ as in (5), if $W_1 \gg W_2$, i.e., the thermal current carried by the phonons is less impeded by thin barriers[11] than the electrical current carried by electrons or holes (as deduced from compaction experiments on polyacetylene by Schweizer,[5,33] although Greig and Sahota[31] found thermal conductivity limited by thin amorphous regions in their polyethylene samples). The fact that S is a zero-current coefficient[7] is not sufficient to ensure that S is dominated by highly conducting regions—the key point is that most of the temperature change must occur across the highly conducting region even if most of the electric potential change occurs across the barriers.

(iii) Heat current carried by elastically scattered electrons. If, further, both heat and electrical currents are carried by the electrons and the Wiedemann-Franz law holds, the thermal resistance of each region is proportional to its electrical resistance R_i, so

$$S = (R_1/R)S_1 + (R_2/R)S_2 \; , \tag{8c}$$

where R is the total resistance. This expression is analogous to the Nordheim-Gorter rule for metallic diffusion thermopower in the presence of different scattering mechanisms[32] and is the relation obtained by substituting the total conductivity or resistance in the Mott formula (1). It is important to note, however, that the derivation of the Mott formula[28] is for a *homogeneous* medium, so this expression [Eq. (8c)] is *not* generally true. The replacement of (8b) by (8c) is sometimes valid for crystalline metals[32] where electrons are the dominant carriers of the heat current, but this is *not* generally the case in polymers.

III. RELATION OF THERMOPOWER TO CONDUCTIVITY

We show our compilation of thermopower data for polymers plotted in Fig. 2 as a function of conductivity. The data available (we plot values for 85 samples) are far less extensive than that for conductivity, but the main trends stand out clearly. The doped polyacetylene samples all show the same general behavior, the room-temperature thermopower decreasing by about 2 orders of magnitude as the conductivity is increased by about 8 orders of magnitude by doping. The correlation between thermopower and conductivity is similar for the different types of dopant. The size of thermopower for both the polypyrrole and polyacene quinone radical (PAQR) polymers tends to lie *below* the values for the doped polyacetylene (one of the PAQR polymers has a negative thermopower, so it is not shown in Fig. 2).

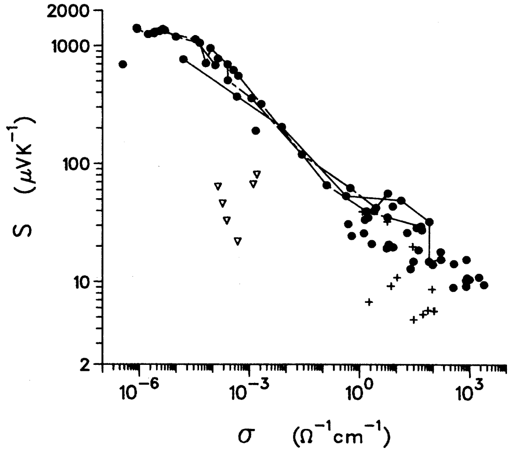

FIG. 2. Compilation of thermopower vs conductivity (at room temperature) for conducting polymers: polyacetylene (circles) doped with $FeCl_4$ (Refs. 7–9), AsF_5 (Refs. 7 and 10–12), I_3 (Refs. 6 and 7), ClO_4 (Ref. 13), or $MoCl_5$ (Ref. 14), polypyrrole (crosses, Refs. 15–17), and polyacene quinone radical polymers (triangles, Ref. 18). The lines connect points for the most extensive data sets.

For conduction by variable-range hopping, the expected thermopower (which is positive for hole conduction) is[34]

$$S_h = \frac{k^2}{2e}(T_0 T)^{1/2} \left. \frac{d \ln N}{dE} \right|_{E_F} \; . \tag{9}$$

T_0 is the parameter appearing in the Mott variable-range-hopping law for the conductivity:

$$\sigma = \sigma_0 \exp[-(T_0/T)^{\gamma}] \; , \tag{10}$$

where σ_0 is not strongly dependent on temperature, and generally $\gamma = \frac{1}{4}$ for three-dimensional conduction, although higher values are possible.[34] As the conductivity increases, the parameter T_0 is found to decrease,[35] as expected since it is inversely related to the localization length.[34] Therefore, the hopping thermopower is also expected to decrease in size, but more slowly than T_0, which is the behavior we find in Fig. 2. If the electrical resistance is dominated by regions in which hopping occurs, due to the presence of disorder or soliton states, it is likely that these regions also make a substantial contribution to thermal resistance and, therefore, thermopower at moderate doping levels. Thus in the framework of the variable-range-hopping expressions, we can qualitatively relate the behavior of the size of S to the corresponding universal behavior of the parameter T_0 as a function of conductivity found by Schäfer-Siebert *et al.*[35] The decrease in thermopower by a factor of about 50 as conductivity increases from 10^{-4} to 10^{2} $\Omega^{-1}\text{cm}^{-1}$ is smaller than might be expected from a $T_0^{1/2}$ dependence, but this could be due to variations in $d\ \ln N/dE$ in (9) or the presence of other contributions to thermopower. Since hopping thermopower becomes small as conductivity increases, a change to metallic thermopower in the most highly conducting samples would produce little discontinuity in the correlation of S with σ.

Comparing (9) to the usual Mott law (1) for a metal, we see that S_h will be larger than that for metals with a similar value of $d\ \ln N/dE$ by a factor $(T_0/T)^{1/2}$. Considering $\sigma \sim 10^{-1}$ $\Omega^{-1}\text{cm}^{-1}$ near the middle of the conductivity range, we have[35] $T_0 \sim 3\times10^{5}$ K, so the factor $(T_0/T)^{1/2}$ is of order 30. From Fig. 2 we find $S \sim 80$ μV/K for this value of conductivity (corresponding to a value of $|d\ \ln N/dE|$ of about 2 eV^{-1}), which since metallic thermopowers are typically a few μV/K is of the expected order of magnitude.

IV. TEMPERATURE DEPENDENCE OF THERMOPOWER

The data available on the temperature dependence of thermopower are rather sparse. In order to have a reasonable temperature range for fitting, we consider only data sets extending from room temperature to below 50 K. Since conductivity becomes very small at low temperatures for lightly doped samples, thermopower becomes very difficult to measure. Consequently, the available data with a wide temperature range are for those polymers of higher conductivity in Fig. 2, so it is these polymers (dopant concentration more than 0.5 mol % and thermopowers less than 100 $\mu\text{V K}^{-1}$) for which we perform fits. The data sets extending below 50 K for polyacetylene doped with FeCl_4 and AsF_5 are listed in Table I. We also mention below limited data for $[\text{CH}(\text{I}_3)_y]_x$ and polypyrrole polymers.

A. Moderately doped samples

The conductivity of moderately doped conducting polymers often[5,6] has a temperature dependence similar to the Mott variable-range-hopping law (10) at low temperatures. The corresponding temperature dependence of thermopower, as indicated by (9), is a $T^{1/2}$ variation. In general agreement with this prediction, the observed increase of thermopower with temperature is typically sublinear. However, the data tend to be intermediate between $T^{1/2}$ and linear behavior, and as shown by the top three curves in Fig. 3, can often be described reasonably well by

$$S = XT + CT^{1/2} . \tag{11}$$

This relation can be viewed as an example of the general expression (8b), combining a hopping term with a linear term from another source (possibly, but not necessarily, metallic conduction). (To compare this expression to the data, we have taken X and C as constants, but effects of their possible temperature dependence are discussed below. We have not included the electron-phonon enhancement term mentioned in Sec. IV B, since this generally produces only a relatively small curvature for realistic parameters and did not result in significant improvements to the fit.)

Values of X and C for $\text{CH}(\text{FeCl}_4)_y$ and $\text{CH}(\text{AsF}_5)_y$ polymers (except those of highest conductivity which are discussed in the next section) are listed in Table I. As

TABLE I. Fit parameters X and λ_{eff} for the thermopower of polyacetylene doped with FeCl_4 and AsF_5 fitted to the expression (12) for metallic thermopower including the effect of the electron-phonon interaction, or X and C for fits to (11) including a $T^{1/2}$ term as from variable-range-hopping conduction (the better of the two fits is listed). Also given are the dopant concentration y, the reference for the source of the data, the magnitude of conductivity σ(300 K) and thermopower S(300 K) near room temperature, and the root-mean-square deviation d per degree of freedom for the fit.

Dopant	y (mol fraction)	Ref.	σ(300 K) ($\Omega^{-1}\text{cm}^{-1}$)	S(300 K) ($\mu\text{V K}^{-1}$)	X ($\mu\text{V K}^{-2}$)	C ($\mu\text{V K}^{-3/2}$)	λ_{eff}	d ($\mu\text{V K}^{-1}$)
			Fits to metallic expression (12)					
FeCl_4	0.0612	7	988	10.5	35.1		0.54	0.28
	0.0593	7	852	10.8	35.6		0.66	0.34
	0.061	7	814	15.5	51.0		0.39	0.29
AsF_5	0.147	10	2450	9.5	31.6		−0.07	0.08
	0.095	10	1800	11.0	38.5		0.05	0.12
	0.1 *cis*	11	800	9.2	32.8		0.26	0.16
	0.1 *trans*	11	800	10.3	34.2		−0.18	0.18
	0.148	7	362	9.0	29.6		−0.08	0.30
			Fits to expression (11) with hopping term					
FeCl_4	0.0378	7	162	18.0	21.6	0.68		0.46
	0.0179	7	36.2	28.7	21.7	1.31		0.62
	0.0106	7	1.7	35.1	23.4	1.73		1.62
	0.0146	8	~6.3	20.8	2.3	1.14		1.02
	0.0069	8	~1.4	33.8	35.3	1.34		1.20
AsF_5	0.002	12	0.5	31.1	72.2	0.76		1.23

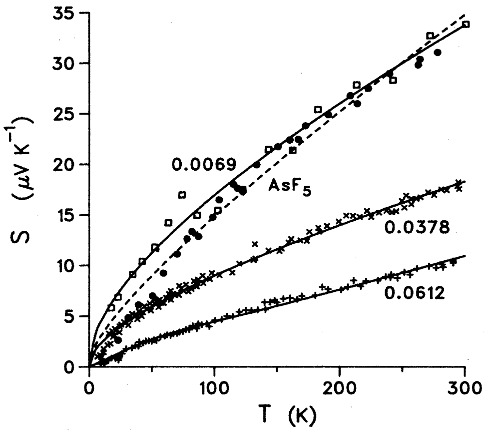

FIG. 3. Thermopower vs temperature for $CH(FeCl_4)_y$ polymers (Refs. 7 and 8), labeled by dopant concentration y, and for $CH(AsF_5)_{0.002}$ (Ref. 12), compared to curves representing the fits of Table I. The curve drawn for $CH(FeCl_4)_{0.0612}$ represents metallic behavior given by (12) with no hopping term; the other curves represent (11) including a hopping $T^{1/2}$ term.

conductivity increases and the total size of thermopower decreases, the coefficient of the hopping term decreases in each of the two series of $FeCl_4$-doped samples, as expected for a trend to more metallic behavior.

In some samples, as in the AsF_5-doped polyacetylene in Fig. 3, there is a tendency for the data to fall *below* the expression (11) at low temperatures. We can suggest two possible causes of this trend.

(i) At low temperatures, paths with a greater fraction of hopping conduction material will have their contribution to thermopower frozen out by the conductivity weighting factor mentioned in generalizing (6) from the fibrillar path to the whole sample. In this case of dissimilar paths, the coefficients will be temperature dependent with the hopping term weighted less heavily at low temperatures.

(ii) Greig *et al.*[36] found that the thermal conductivity of their disordered polymers was much less than that of semicrystalline polymers at room temperature, but there was little difference at low temperatures. Thus the thermopower from disordered regions, according to (8b), is weighted more heavily at high temperatures than at low temperatures, leading to a reduction of thermopower at low temperatures towards the value characteristic of the crystalline material.

Park *et al.*[7] have shown that their measured thermopower for a $CH(I_3)_{0.073}$ sample was reasonably well described by (11). However, other samples[6] gave a thermopower showing closer to linear behavior even though they were more lightly doped and the size of room-temperature thermopower was, as expected, larger.

For their polypyrrole samples, Shen *et al.*[15] and Maddison *et al.*[17] found that the conductivity followed the Mott law (10), and found a thermopower very approximately linear in temperature (at least up to about 220 K) but in some cases not extrapolating to $S=0$ as T tends to zero. This behavior is generally consistent with a linear term and a small hopping term. Aged samples[16] showed a change in sign to negative thermopowers at low temperature. A possible cause of this behavior could be cancellation effects between electron and hole contributions to thermopower of different signs, the total thermopower depending on the balance of the contributions, which may be temperature dependent. Such cancellation could also account for the low magnitude of thermopower.

B. High-conductivity samples

For the highest-conductivity polymers, there is a fundamental change in the behavior of the conductivity as temperature tends to zero: σ remains finite[10,11] as for metals, instead of tending to zero as in the variable-range-hopping law. If conduction is largely metallic except for tunneling across thin heat-conducting barriers,[5] thermopower should be dominated by metallic behavior, as mentioned above. Park *et al.*[7] found that the thermopower changed shape, becoming more linear, sometimes with an increase of slope below about 50 K. This "knee" at about 50 K is remarkably similar to the behavior seen in many disordered metals,[29] as illustrated in Fig. 4(b), and ascribed to the electron-phonon enhancement of diffusion thermopower at low temperatures. The phonon-drag peak, which dominates the temperature dependence of thermopower below room temperature in most good crystals, is suppressed by disorder,[29] leaving the enhancement effect in diffusion thermopower visible as a decrease in slope as temperature increases and the enhancement decays on the scale of the Debye temperature.

The Mott formula for thermopower (1) applies only for the energy-dependent conductivity function $\sigma(E)$ varying slowly near the Fermi level. To take account of the effect of the electron-phonon interaction on diffusion thermopower, it is necessary to go back to the more general expression,[28] obtaining[29]

$$S_d = X[1+\lambda_{\text{eff}}\bar{\lambda}_S(T)]T , \tag{12}$$

where λ_{eff} is the effective enhancement for thermopower at zero temperature, and the decay of enhancement as temperature increases is given by the function

$$\bar{\lambda}_S(T) = \frac{\int_0^\infty E^{-1}\alpha^2F(E)G_S\left[\frac{E}{kT}\right]dE}{\int_0^\infty E^{-1}\alpha^2F(E)dE} . \tag{13}$$

Here $\alpha^2F(E)$ is the Eliashberg function and $G_S(y)$ is a universal function defined previously.[29] In the absence of a detailed knowledge of $\alpha^2F(E)$ in the conducting polymers, but noting that the specific heat of heavily doped samples at low temperatures[37] has a T^3 term, we use a Debye model, i.e., $\alpha^2F(E)$ increasing with phonon energy E as E^2 up to a Debye cutoff corresponding to effective Debye temperature T_D^*. Fortunately, the shape of $\bar{\lambda}_S(T)$ is not very sensitive to the model assumed.[38] The temperature dependence of the thermopower enhancement is then determined except for the scale factor T_D^*. It is difficult to estimate an effective Debye temperature from the specific heat of polymers, since a large contribution comes from localized modes, which may not couple so strongly to the conduction electrons. Moses *et al.*[37] found a transverse-mode effective Debye temperature of 220 K in undoped polyacetylene, while Mermilliod and Zuppiroli[39] suggested a Debye temperature of about 500 K for acoustic modes in undoped and lightly doped samples. We have used the value $T_D^* = 300$ K in the calculations, although values from 200 to 500 K also give reasonable fits to thermopower.

We show in Fig. 4 the fits of our metallic thermopower expression (12) to two of the highly conducting polymers, with a fit for a glassy metal shown for comparison. The good agreement of the polymer data with the calculation indicates that the electron-phonon interaction should be considered as a possible source of the thermopower nonlinearity in these polymers. We list in Table I the fitting parameters for all the polymers that follow the metallic model (12) more closely than the expression (11) containing a hopping term. These polymers are found to be those with conductivities in excess of 300 $\Omega^{-1}\,\mathrm{cm}^{-1}$ and finite conductivity in the zero-temperature limit—this fact supports the suggestion that the nonlinearities in Fig. 4(a) may be due to the metallic electron-phonon effect. However, the predicted nonlinearities due to a hopping contribution and to electron-phonon enhancement are unfortunately rather similar, so further data are needed, particularly at low temperatures where the predictions are more different ($T^{1/2}$ for hopping and approximately linear for the electron-phonon interaction).

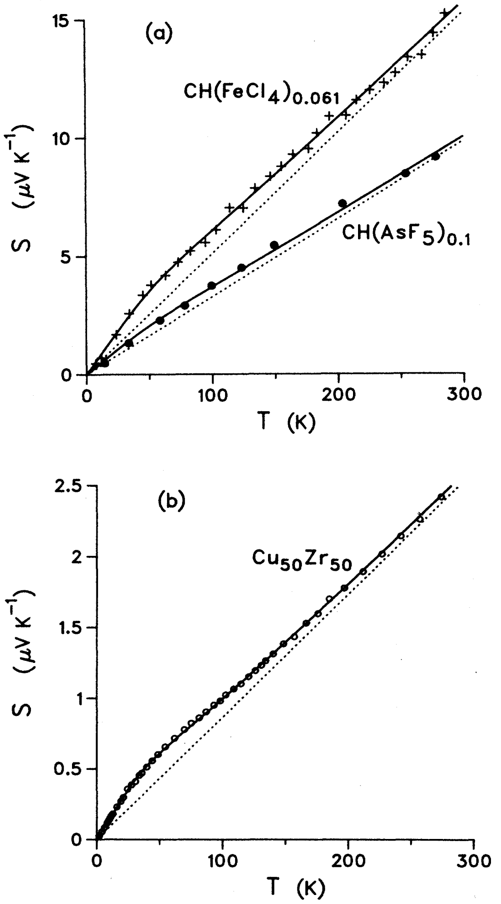

FIG. 4. (a) Thermopower for two of the most highly conducting polymers $\mathrm{CH(FeCl_4)_{0.061}}$ (crosses, Ref. 7) and *cis* $\mathrm{CH(AsF_5)_{0.1}}$ (dots, Ref. 11) fitted to our expression (12) for metallic diffusion thermopower (solid lines), with parameters listed in Table I. The dotted lines show the bare linear thermopower for each fit. (b) Similar fit showing the electron-phonon enhancement effect for the thermopower of the amorphous metal $\mathrm{Cu_{50}Zr_{50}}$ (Ref. 38), with parameters $X = 8.7$ nV K^{-2}, $\lambda_{\mathrm{eff}} = 0.6$, and $T_D = 200$ K.

The values of λ_{eff} for $\mathrm{CH(FeCl_4)}_y$ polymers are similar to those in many metals, suggesting a similar coupling between delocalized conduction electrons and phonons in our model. The interaction in $\mathrm{CH(AsF_5)}_y$ polymers would be very small, with the thermopower of the highly doped samples being fairly close to linear. In some cases the value of λ_{eff} is negative. Such behavior is seen[40] in Ag-Sn films, in which thermopower is small. It can arise when the enhancement effect is small enough (for example, because the bare thermopower XT is very small) to be counteracted by velocity and relaxation time renormalization,[29] which have approximately the same temperature dependence as the enhancement but may have opposite sign.

Possible alternative explanations of nonlinearity in metallic thermopower are phonon drag and scattering by magnetic impurities[7] (the Kondo effect). Phonon drag is suppressed[27] in glassy metals with conductivities less than 200 $\Omega^{-1}\,\mathrm{cm}^{-1}$ and electronic mean free paths less than about 15 Å. Although considerable disorder is present in many polymers,[5] one might expect phonon-drag thermopower to become significant in crystalline polymers with relatively large thermal conductivity and electronic mean free paths. The expected temperature dependence follows that of the lattice heat capacity at low temperatures, i.e., as T^3 in highly doped polymers,[37] in contrast to the linear dependence arising from electron-phonon enhancement. Thus accurate low-temperature measurements should help to investigate this possibility, as well as that of a remaining hopping contribution. The Kondo or spin-fluctuation peak in thermopower, which of course occurs only in systems containing Fe or other magnetic impurities, is typically seen at very low temperatures, below the temperature of the phonon-drag peak, and is also washed out by disorder.[41] Clear observation of the nonlinearity in polymers without magnetic impurities would eliminate this possibility.

The thermopower due to elastic tunneling across a potential barrier between metals is small, since conduction occurs in the vicinity of the Fermi level and the thermopower should generally follow an approximately linear trend with a size determined by the energy dependence of the density of states on either side of the barrier and the tunneling matrix elements. The thermopower contribution from fluctuation-induced tunneling across potential barriers between metallic regions is not given,[42] but could be less simple.

V. CONCLUSION

Our analysis of transport in heterogeneous media and in metallic systems contributes to a framework for the interpretation of the thermopower of highly conducting polymers. In particular, limitations on the validity of previous treatments of thermopower in heterogeneous media have been pointed out.

We find that the behavior of the magnitude of the thermopower and its temperature dependence for samples with up to a few percent doping is generally consistent with a major contribution from variable-range-hopping conduction or a similar mechanism, as has been found for the conductivity. The magnitude of thermopower as a function of conductivity for doped polyacetylene follows a well-defined trend that is consistent with the analogous trend of the Mott variable-range-hopping parameter T_0 found from conductivity by Schäfer-Siebert *et al.*[35] As the doping increases, the thermopower tends to become more linear in temperature as the size of the fitted $T^{1/2}$ term decreases, as expected for a trend towards metallic behavior.

Once the conductivity has changed (as doping level increases) so that it remains finite as $T \rightarrow 0$ (rather than diverging as for hopping conduction), there is also evidence of some change in thermopower shape in that no hopping term is required. We find that the thermopower in this case can be fitted rather well by the expression (12) for metallic thermopower alone (including the effect of the electron-phonon interaction). Metallic thermopower, even in the absence of phonon drag, is generally *not* linear in the presence of the electron-phonon interaction, instead showing just the kind of nonlinearity seen in the $FeCl_4$ and AsF_5 doped polyacetylene in Fig. 4(a). Such behavior is widely seen in disordered metals, but is camouflaged in crystalline metals by larger nonlinearities due to phonon drag. The observation of the thermopower "knee" at about 50 K (where it is expected for typical Debye temperatures) for four of the most highly conducting polymer samples, and the good quantitative fit of the data to the calculated thermopower shape, are arguments in favor of a significant nonlinearity due to the electron-phonon interaction in these cases. However, so far the data are very limited and further measurements, especially accurate low-temperature measurements on very high conductivity samples, are of great interest.

If the thermopower nonlinearities in "metallic" polymers *are* identified as due to electron-phonon enhancement of thermopower, they could be used to derive information about the strength and temperature dependence of the conduction electron-phonon interaction. If thermopower is proportional to temperature, on the other hand, this is a noteworthy result indicating a very small electron-phonon interaction (or possibly a cancellation effect if thermopower is very small). Thermopower can therefore help show whether the electron-phonon interaction is similar to that in metals, or whether it is partially suppressed due to preferential conduction along chains;[43] such suppression could imply very high values of intrinsic conductivity, since metallic resistivity at room temperature is proportional to the size of the electron-phonon interaction.

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