Conductivity, thermopower, and statistical shift in amorphous semiconductors

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The temperature dependence of the thermopower and thermally activated conductivity is reflecting both the statistical shift of the Fermi level and the variation of the energy at which the transport mainly takes place. In amorphous semiconductors the two components are of comparable importance. It is shown that these contributions can be separated from each other by taking advantage of a simple relation between conductivity and thermopower, which has been disregarded so far. This discrimination allows us to extract new and more detailed information on the conduction mechanism, on the density of states, and on the position of the Fermi level from experimental data. In particular, the contribution to the transport at any energy may be obtained from a Laplace transformation of the temperature-dependent prefactor of the thermally activated conductivity. The analysis of data from samples with different amount of doping, which will be presented as an example, is of particular interest because of the information on doping-induced changes of mobility and density of states in the energy region where the transport takes place.

I. INTRODUCTION

One of the most remarkable differences between transport in amorphous and in crystalline semiconductors is the contribution from hopping between localized states, which may involve the whole range of energies of the mobility gap in the case of amorphous semiconductors with a high gap density of states.[1,2] As a consequence the energy at which the dominant transport processes take place can vary drastically with temperature, as opposed to relatively small changes of only a few kT in the case of crystalline semiconductors. In the current literature on amorphous semiconductors this fact has been taken into account in the interpretation of experimental data in terms of simple *ad hoc* models in which the contributions to the total transport are split into thermally activated hopping with lower and band conduction with higher activation energy[1,3-6] (and, possibly, variable range hopping near the Fermi level,[7] dominating at low temperatures or/and large density of states near ϵ_F). A major difficulty with this kind of analysis arises from the additional temperature dependence of the transport properties which originates from the statistical shift of the Fermi level, and which could not be properly separated from the above-mentioned dependences in former work. Also it appears somewhat unsatisfactory to start the analysis from a rather crude model, which nevertheless involves assumptions which may be too restrictive to reflect the real situation.

The purpose of this paper is to show that it is possible to separate the two components which determine the temperature dependence of the transport properties within the framework of a simple, but nevertheless sufficiently general, model. This possibility results from a simple relation between conductivity and thermopower which had not been taken into account so far. As a result not only quantitative information on the temperature shift of the energy of the dominant contribution to the transport and of the position of the Fermi level may be obtained, but the analysis even yields the differential conductivity $\sigma(\epsilon)$, i.e., the contribution to the transport at any energy.

Doped amorphous semiconductors are of particular interest with respect to our approach. The distinction between transport changes due to a shift of the Fermi level and those due to changes of the density of states and of the mobility provides a deeper understanding of the effect of doping and allows one to check the validity of assumptions which are widely used.

In the theoretical part of this paper we derive the expressions which relate the quantities which determine the transport properties in our model, such as density of states $N(\epsilon)$, energy-dependent mobility $\mu(\epsilon)$, and amount of doping, to the experimentally observed quantities, i.e., conductivity $\sigma(T)$ and thermopower $S(T)$. In the second part we analyze and discuss some experimental data as an example.

II. MODEL ASSUMPTIONS AND THEORY

We want to use a model of an amorphous semiconductor which is as general as possible, whose features are based only on a few assumptions, and which includes currently used models as special cases.

The first assumption concerns the density-of-states distribution $N(\epsilon)$ (see Fig. 1). We assume that $N(\epsilon)$ does not depend on the amount of doping and that doping only shifts the position of the Fermi level $\epsilon_F(T; n_{D,A})$ according to the change of elec-
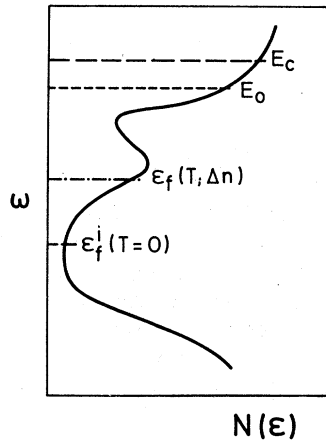
FIG. 1. Density-of-states distribution of an amorphous semiconductor, schematically. The position of the Fermi level is $\epsilon_F^i(T=0)$ for the undoped material at zero temperature and $\epsilon_F(T; \Delta n)$ for the semiconductor with an effective donor concentration of Δn at finite temperature T. E_0 is an arbitrarily chosen energy in the conduction-band tail used as reference energy instead of E_c, since the position of the mobility edge E_c is unknown.

tron concentration by doping, which is

$$\Delta n = \begin{cases} n_D, & \text{for } n \text{ doping} \\ -n_A, & \text{for } p \text{ doping} \end{cases} \tag{1}$$

where n_D and n_A are the concentration of effective donors and acceptors, respectively. The position of the Fermi level $\epsilon_F(T; \Delta n)$ at a given temperature and a given doping follows from

$$\Delta n = \int_{-\infty}^{\infty} d\epsilon\, N(\epsilon) f(\epsilon - \epsilon_F(T; \Delta n))$$

$$- \int_{-\infty}^{\epsilon_F^i(T=0)} d\epsilon\, N(\epsilon), \tag{2}$$

where

$$f(\epsilon - \epsilon_F) = \{\exp[\beta(\epsilon - \epsilon_F)] + 1\}^{-1} \tag{3}$$

is the Fermi-Dirac distribution function and $\epsilon_F^i(T=0)$ is the Fermi level at zero temperature in the undoped amorphous semiconductor $[\beta = (kT)^{-1}]$.

The assumption of a doping-independent density-of-states distribution $N(\epsilon)$ is expected to represent a good approximation for not too high doping levels.

Our second assumption refers to the transport properties of the amorphous semiconductor. We write the conductivity in the form[1,8,9] (in the following we consider only conduction by electrons; the generalization to include holes is trivial)

$$\sigma(T; n_D) = e \int_{-\infty}^{\infty} d\epsilon\, N(\epsilon)\mu(\epsilon) f(\epsilon - \epsilon_F(T; n_D)). \tag{4}$$

This form for σ, which differs from familiar ex-

pressions by the neglect of a statistical factor for the final state of scattering processes, is justified if the mobility is substantially different from zero only at energies $\epsilon - \epsilon_F \gg kT$. In this case the final states in the scattering processes which determine the mobility $\mu(\epsilon)$ are practically always empty independently on whether scattering is between localized states (hopping) below, or between extended states (band conduction) above the mobility edge E_c.

As the significance of the mobility edge for separating extended from localized states will not be particularly important in the following we introduce E_0 as some reference energy in the density-of-states distribution $N(\epsilon)$. With our assumptions one may rewrite (4) as

$$\sigma(T; n_D) = \sigma_0(T) \exp\{-\beta[E_0 - \epsilon_F(T; n_D)]\} \tag{5}$$

with

$$\sigma_0(T) = e \int d\epsilon\, N(\epsilon)\mu(\epsilon) \exp[-\beta(\epsilon - E_0)]. \tag{6}$$

In the following we will write the temperature-dependent prefactor $\sigma_0(T)$ in the form

$$\sigma_0(T) = \sigma_{00} \exp[-\beta V(T)] \tag{7}$$

for reasons which will become evident soon. The purpose for writing $\sigma(T; n_D)$ in a form as given in (5) is a factorization into a part $\exp\{-\beta[E_0 - \epsilon_F(T; n_D)]\}$ which depends on the position of the Fermi level, and, hence is doping dependent, and another one, $\sigma_0(T)$, which is doping independent in our model.

The corresponding expression for the Peltier coefficient Π (which is related to the thermopower S by the Onsager relation $\Pi = eST$) is[8-11]

$$-\Pi(T) = \int d\epsilon\, N(\epsilon)\mu(\epsilon)[\epsilon - \epsilon_F(T; n_D)]$$

$$\times f(\epsilon - \epsilon_F(T; n_D))/\sigma(T; n_D). \tag{8}$$

In a similar way as before, (8) may be rewritten in the form

$$-\Pi(T) = W(T) + E_0 - \epsilon_F(T; n_D). \tag{9}$$

Here the contribution

$$W(T) = e \int d\epsilon\, N(\epsilon)\mu(\epsilon)(\epsilon - E_0) \exp[-\beta(\epsilon - E_0)]/\sigma_0(T) \tag{10}$$

to the total average energy transported per charge carrier is again a doping-independent quantity.

For our analysis below it will be of great advantage that $W(T)$ and $V(T)$ from (10) and (7) are related to each other in a very simple form. Using (7) and (6) one verifies by differentiation that

$$d(\beta V)/d\beta \equiv V(T) + \beta(dV/d\beta) = W(T). \qquad (11)$$

This simple relation results from the assumption that the mobility $\mu(\epsilon)$ in (5) and (10) does not depend on temperature. This approximation is probably justified at not too low temperatures in view of the fact that the dominant temperature dependence of the integrand in (5) and (10) comes from the Boltzmann factor $\exp[-\beta(\epsilon - E_0)]$.

An additional term appears in the expression (11), if the variation of $\mu(\epsilon)$ with temperature is taken into account:

$$d(\beta V)/d\beta \equiv V + \beta(dV/d\beta) = W(T) + X(T) \qquad (11')$$

with

$$X(T) = ekT^2 \int d\epsilon\, N(\epsilon)\mu(\epsilon)[d\ln\mu(\epsilon)/dT]$$

$$\times \exp[-\beta(\epsilon - E_0)]/\sigma_0(T). \qquad (12)$$

From a qualitative picture for the temperature dependence of $\mu(\epsilon)$,[12] as shown schematically in Fig. 2 we expect a positive or negative sign of $X(T)$ depending on whether the increase of hopping mobility for energies below E_c or the decrease of mobility in extended states above E_c dominates.

It is well known that both the Peltier coefficient Π and the activation energy of the conductivity, defined as the negative slope of $\ln\sigma$ vs $\beta = (kT)^{-1}$ give information about the distance between the energy where the transport takes place and the Fermi level. There is, however, a difference between the variation of the Peltier coefficient and of the activation energy with temperature.

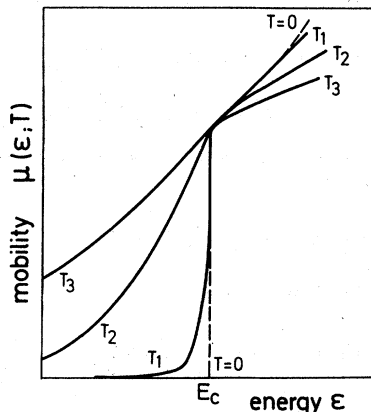In crystalline semiconductors this difference is

FIG. 2. Mobility $\mu(\epsilon; T)$ of a carrier at the energy ϵ for different temperatures $T_3 > T_2 > T_1 > 0$, normalized to the value at $E = E_c$, with a finite step of $\mu(\epsilon; 0)$ assumed for $\epsilon = E_c$, schematically. The increasing electron-phonon interaction at higher temperatures stimulates activated hopping processes below E_c, but reduces the mobility in extended states above E_c.

rather small. In discussions of the Peltier coefficient a linear $W(T)$ of the order of kT, corresponding to the average kinetic energy transported by the Bloch electrons is usually included. The temperature dependence of $\sigma_0(T)$ which is related to $V(T)$ by (7), reflects the influence of the various scattering processes.

In amorphous semiconductors one expects, depending on temperature, dominant contributions to Π and σ either from hopping in tail states quite far below E_c or from band conduction above E_c.[1,3-6] As a consequence much larger shifts of the average energy transported per carrier are expected than in crystalline semiconductors. Thus, large changes of $W(T)$ and at the same time also of $\sigma_0(T)$ should result. The latter lead to changes of $V(T)$ comparable in magnitude, but opposite in sign to those of $W(T)$. From these considerations it is quite obvious, that rather detailed information about the transport processes in amorphous semiconductors may be obtained if $W(T)$ and $V(T)$ are known as a function of temperature.

Of course, $W(T)$ or $V(T)$ cannot be deduced directly from measurements of $\Pi(T)$ or $\sigma(T)$, respectively, since in both cases the energy is measured with reference to the Fermi level, which itself, also varies with temperature. This "statistical shift" of the Fermi level, however, also contains important information about the amorphous semiconductor, namely, about its density-of-states distribution $N(\epsilon)$. Fortunately, however, the differences between Peltier coefficient and activation energy allow one to separate the statistical shift $d\epsilon_F/dT$ from $W(T)$ and $V(T)$. To the knowledge of the present author no systematic analysis of this possibility has been performed so far. Therefore, we want to show in the following paragraphs how the quantities $\epsilon_F(T)$, $W(T)$, and $V(T)$ may be extracted from $\Pi(T)$ and $\sigma(T)$.

From (5) and (7) we obtain for the differential "activation energy" at a temperature $T = (k\beta)^{-1}$

$$-d\ln\sigma/d\beta = V(T) + E_0 - \epsilon_F(T) + \beta(dV/d\beta - d\epsilon_F/d\beta).$$

$$(13)$$

This activation energy differs from the Peltier coefficient Π, given by (9), by

$$-d\ln\sigma/d\beta + \Pi = V - W + \beta(dV/d\beta) - \beta(d\epsilon_F/d\beta). \qquad (14)$$

The expression (14) reduces to

$$-d\ln\sigma/d\beta + \Pi = -\beta(d\epsilon_F/d\beta) = T(d\epsilon_F/dT) \qquad (15)$$

if (11) holds. [Otherwise the quantity $X(T)$ from (11'), given by (12), has to be added on the right-hand side of (15).]

Thus, the difference between differential activation energy and the Peltier coefficient in this case

provides the shift of the Fermi level with temperature directly, independent of $W(T)$ and $V(T)$, whence

$$\epsilon_F(T; n_D) = \epsilon_F(T_1; n_D)$$
$$+ \int_{T_1}^{T} dT' [(d\ln\sigma/d\beta' - \Pi)/T'] . \quad (16)$$

On the other hand, we see that the difference between the negative logarithm of the conductivity and the thermopower S in the appropriate scale $eS/k = \Pi/kT$ provides, apart from the prefactor σ_{00} [see (7)] the difference between W and V:

$$\ln\sigma - eS/k = \ln\sigma_{00} + \beta[W(T) - V(T)] . \quad (17)$$

This is an important result since the difference $W(T) - V(T)$ is independent of the position of the Fermi level. Hence, $\ln\sigma - eS/k$ is a doping-independent quantity and should be the same function of temperature for a set of amorphous semiconductors which differ only by the amount of doping. Therefore it allows us to test the validity of our assumption that $N(\epsilon)$ and $\mu(\epsilon)$ is not influenced by doping by comparing $\ln\sigma - eS/k$ for different samples. It should be pointed out that this possibility does not depend on whether (11) holds or not.

In addition, we can obtain $W(T)$ and $V(T)$ separately after integration of $dV/d\beta$, if the condition for the validity of (11) holds

$$V(T) = V(T_0) + \int_{\beta_0}^{\beta} d\beta' \{[W(T') - V(T')]/\beta'\} . \quad (18)$$

We remember that the question whether relation (11) holds is equivalent to the question whether the change of $\mu(\epsilon)$ with temperature, averaged over all energies with the statistical weight $N(\epsilon)\exp(-\beta\epsilon)$, as given by $X(T)$ from (12), can be neglected. With our present knowledge about transport in amorphous semiconductors one can hardly do more than speculate with qualitative arguments resulting from a picture as shown in Fig. 2. Experimentally, however, one may obtain the answer from $\Pi(T)$ and $\sigma(T)$ if $N(\epsilon)$ is known from some other experiments like field effect[13] or capacitance-voltage measurements,[14] or from the shift of ϵ_F as a function of doping. The knowledge of $N(\epsilon)$ allows a calculation of the statistical shift $d\bar\epsilon_F/dT$. If this statistical shift differs from the result obtained from (15) this difference should correspond to the term $X(T)$ from (11') which has been omitted on the right-hand side of (15). Needless to say that one expects the same function $X(T)$ at different doping levels from our model as $X(T)$ is defined as a doping-independent quantity. Going back to the definition of $V(T)$ and $W(T)$ as given by (7) and (6) and by (10), respectively, we remember that $V(T)$ is directly related to the tem-

perature-dependent prefactor $\sigma_0(T)$ of the conductivity by

$$\sigma_0(\beta) = \sigma_{00} \exp(-\beta V)$$
$$= \int_{-\infty}^{\infty} d\epsilon \, \sigma(\epsilon) \exp[-\beta(\epsilon - E_0)] , \quad (19)$$

where we have defined the differential conductivity $\sigma(\epsilon)$ by

$$\sigma(\epsilon) = eN(\epsilon)\mu(\epsilon) . \quad (20)$$

The argument β instead of T has been used in (19) in order to visualize that this prefactor $\sigma_0(\beta)$ is, apart from a trivial shift of the reference energy E_0, the Laplace transform of the differentical conductivity $\sigma(\epsilon)$, provided that the temperature dependence of $\sigma(\epsilon)$ may be neglected, and $\sigma(\epsilon)$ vanishes fast enough for $\epsilon \to -\infty$. Thus, backtransformation of $\sigma_0(\beta)$ gives $\sigma(\epsilon)$, i.e., the full information about the contribution to the transport at each energy. It is unnecessary to emphasize that the knowledge of $\sigma(\epsilon)$ and possibly of its dependence on doping may enable us to obtain a much deeper insight into the transport phenomena in amorphous semiconductors.

III. COMPARISON WITH EXPERIMENTS AND CONCLUSIONS

Experimental results on both conductivity and thermopower for a set of amorphous glow-discharge silicon samples with different amount of n doping have been presented by the Marburg group.[4]

In Fig. 3 the curves $\ln\sigma$ and eS/k vs T^{-1} are plotted together for their samples, numbered 1 to 7 corresponding to increasing amount of doping. The two sets of curves are shifted vertically such that the zero of eS/k coincides with $\ln\sigma_{00}$. Thus, it follows from (17), that the difference between corresponding $\ln\sigma$ and eS/k values gives directly $\beta(W - V)$.

The value of σ_{00} was obtained from the $\beta = 0$ axis intercept of tangents to the low-temperature part of the $\ln\sigma$ curves. The tangents at low temperatures are chosen for two reasons. First, the statistical shift of the Fermi level may be neglected at low temperatures. Second, one can see from the equation for a tangent at $\beta_0 = (kT_0)^{-1}$:

$$\ln\tilde\sigma = \ln\sigma_{00} + \beta_0^2(dV/d\beta - d\epsilon_F/d\beta)_{\beta_0}$$
$$- [V + E_0 - \epsilon_F + \beta \, d(V - \epsilon_F)/d\beta]_{\beta_0}\beta \quad (21)$$

that there is, in addition to the statistical shift $\beta_0^2(d\epsilon_F/d\beta)_{\beta_0} = -(d\epsilon_F/dkT)_{T_0}$ another contribution $\beta_0^2(dV/d\beta)_{\beta_0} = -(dV/dkT)_{T_0}$ to the $\beta = 0$ intercept. This contribution, however, can become zero, if β_0 is chosen to coincide with the intercept of $\ln\sigma$ with eS/k, which corresponds to $W - V = 0$. Thus
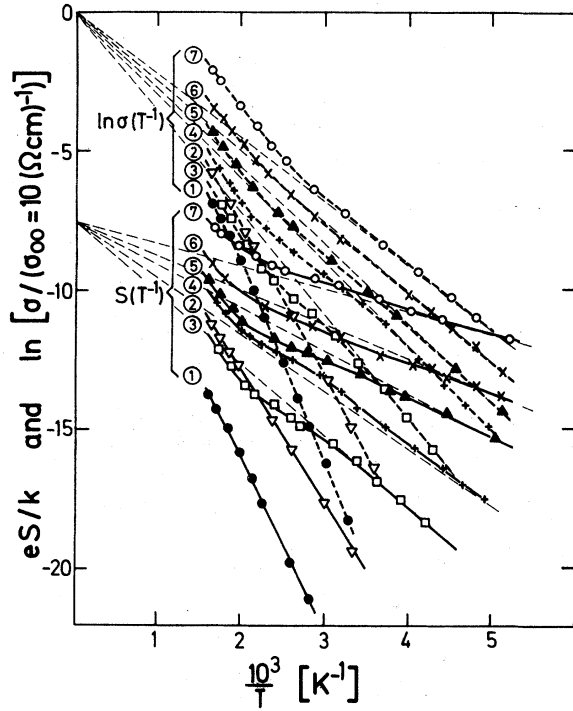
FIG. 3. Experimental results for the thermopower S and the conductivity σ for glow-discharge silicon from Ref. 4 plotted together. The amount of n-doping was estimated to increase from sample 1 to 7 from 0 to 10^{19} cm^{-3}.
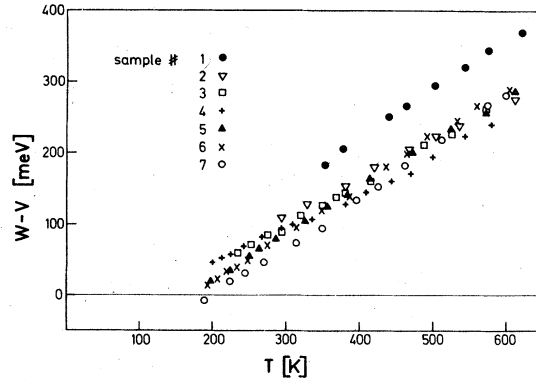

FIG. 4. $W - V$, defined by Eq. (10) and (7), obtained from the set of experiments shown in Fig. 3. The results for different samples, apart from those for sample 1 agree reasonably well. For a discussion of systematic changes with increasing amount of doping see text.

$(\beta dV/d\beta)_{\beta_0} = 0$, at least, if (11) holds, and the intercept of the tangent (21) with the $\ln\sigma$ axis really corresponds to σ_{00} as defined $\approx$ (7).

Three observations should be pointed out: (i) The temperature $T_0 = (k\beta_0)^{-1}$ for which $W - V = 0$, should be the same for all samples if our assumption of $N(\epsilon)$ being doping independent was allowed. Obviously, this is true only as an approximation. With increasing doping T_0 shifts from about 100 to 200 K. (ii) A common value of $\sigma_{00} \approx 10$ (Ω cm)$^{-1}$ is more or less compatible with the data of all samples. For samples 1 and 2, however, σ was too low for measurements down to T_0, which introduces, of course, a considerable amount of arbitrariness in the determination of T_0 by extrapolation of the measured $\ln\sigma$ and eS/k curves. (iii) The tangents to the eS/k curves also have approximately a common intercept with the $\beta = 0$ axis, which corresponds to $eS/k \approx -7.5$. From the equation of these tangents,

$$e\tilde{S}/k = [\beta^2(dW/d\beta - d\epsilon_F/d\beta)]_{\beta_0}$$

$$- [W + E_0 - \epsilon_F + \beta(dW/d\beta - d\epsilon_F/d\beta)]_{\beta_0}\beta, \quad (22)$$

we identify this value with $\beta_0^2(dW/d\beta)_{\beta_0} = -(dW/dkT)_{T_0}$ since we assumed $\beta_0(d\epsilon_F/d\beta)_{\beta_0}$ to be negligible.

In Fig. 4 the $W - V$ values, as obtained from the difference between $\ln(\sigma/\sigma_{00})$ and eS/k in Fig. 3 are plotted vs T. $W - V$ should be the same function of T for all samples, as mentioned in Sec. II, if $N(\epsilon)$ and $\mu(\epsilon)$ were independent of doping for the range of relevant energies. The curves, indeed, agree reasonably well (except for sample 1), but there is clearly a tendency of increasing slope and increasing T_0 at higher doping level. This observation indicates that the assumption of doping-independent $N(\epsilon)$ and $\mu(\epsilon)$ does not apply strictly to actual amorphous semiconductors.

To proceed further let us assume that the condition for the validity of (11) is fulfilled, i.e., that $X(T)$ defined in (12) can be neglected. The most convenient procedure to obtain the quantities $W(T)$, $V(T)$, and $\epsilon_F(T)$ for the various samples is to determine first $\epsilon_F(T) - \epsilon_F(T_1)$ by integration of $d\epsilon_F/dT$ as obtained from the difference between the differential activation energy $d\ln\sigma/d\beta$ and the Peltier coefficient $\Pi = eST$, according to Eq. (15).

The results for $\epsilon_F(T) - \epsilon_F(T_1 = 620$ K), presented in Fig. 5, show qualitatively the behavior which one expects: a rather small shift for the nearly undoped and the weakly doped samples with ϵ_F far below E_0; a particularly strong shift for intermediate doping, where ϵ_F presumably lies in or close to a region of large changes $dN(\epsilon)/d\epsilon$ of the density of states; and, finally, at high doping, there is again only a minor shift, since $N(\epsilon_F)$ is expected to be large, but $[dN(\epsilon)/d\epsilon]_{\epsilon_F}$ relatively small.

In Fig. 6 the results for $\epsilon_F(T) - \epsilon_F(620$ K) were used to obtain $W(T)$ and $V(T)$ from $\Pi(T)$ and $\ln[\sigma(T)/\sigma_{00}]$ according to (9) and (17), respective-
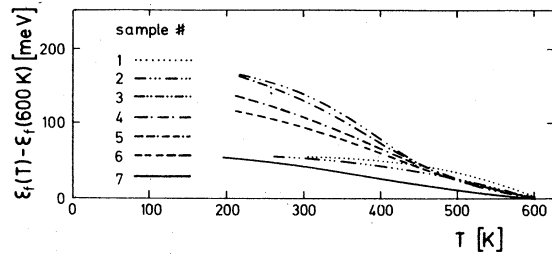
FIG. 5. Statistical shift for the same set of samples as before, obtained by numerical integration of $d\epsilon_F/dT$ according to Eq. (16).

ly. If we write (9) and (17) in the form

$$W(T) = -[E_0 - \epsilon_F(T_1)] - \Pi(T) + [\epsilon_F(T) - \epsilon_F(T_1)] \quad (23)$$

and

$$V(T) = -[E_0 - \epsilon_F(T_1)] - \ln[\sigma(T)/\sigma_{00}] + [\epsilon_F(T) - \epsilon_F(T_1)] \quad (24)$$

we observe, that the constants $E_0 - \epsilon_F(T_1)$ are still undetermined. Indeed, E_0 was only defined as some reference energy without any particular sig-
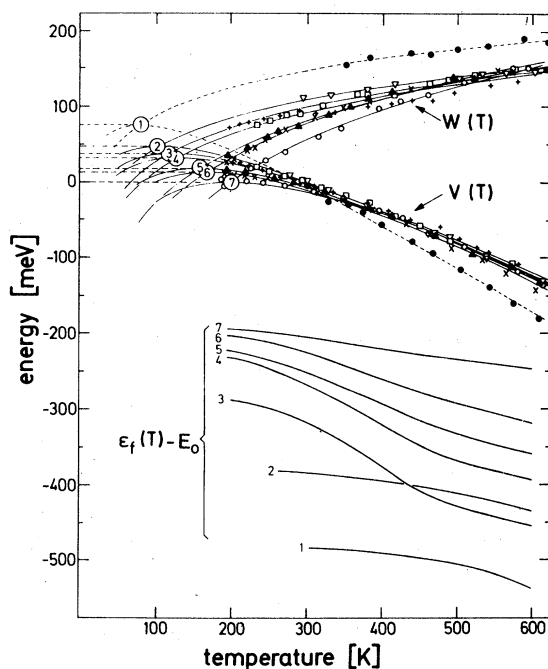

FIG. 6. $W(T)$ and $V(T)$, defined by (10) and (7), respectively, and position of the Fermi level $\epsilon_F(T)$ as obtained from our analysis of the set of data from Ref. 4. $W(T)$ depicts the shift of the transport processes to higher energies with increasing temperature. $V(T)$ is directly related to the temperature dependent prefactor $\sigma_0(T)$ by (7). Full lines for $W(T)$ and $V(T)$ were obtained from a fit to the experimental data according to (27) and (26), respectively.

nificance.

The values of $E_0 - \epsilon_F(T_1)$ for all the other samples would follow immediately once E_0 was chosen for one of them, if $W(T)$ and $V(T)$ really were doping independent. Since this is not strictly the case we have chosen $\epsilon_F(T_1)$ for the different samples such that $W(T)$ and $V(T)$ agree at high temperatures for all samples. This was done for two reasons. First, it appears reasonable that the influence of doping on $N(\epsilon)$ and $\mu(\epsilon)$ is more pronounced in the low-temperature range, when hopping in low-lying tail states dominates (one might think about the effect of additional impurity band states, e.g.), than at high temperatures, where band conduction is generally assumed. Second, it is actually the high-temperature region where the experimental $W(T) - V(T)$ values are nearly doping independent (only sample 1 does not fit into this scheme).

It should be emphasized that the quantities $W(T)$, $V(T)$, and $\epsilon_F(T)$ have been obtained for each one of the samples directly from experiment without any particular model assumptions. In contrast to our treatment, the analysis by other authors started from models with rather specific assumptions on the transport mechanism without taking full advantage of the information contained in the experimental data.[3-6] Thus, for instance, a quadratic energy dependence of $\mu(\epsilon)N(\epsilon)$ in the hopping region was postulated in the analysis by Beyer, Mell, and Overhof,[4] whereas the linear approximation for the statistical shift $d\epsilon_F/dT = 2.9k$ from the work of Spear and Le Comber[13] was used in Friedman's analysis.[5]

In the following we want to analyze first $W(T)$ and $V(T)$ with respect to information on the transport mechanism and its dependence on doping. Subsequently we will shortly discuss the statistical shift for the various samples.

The rather steep increase of $W(T)$ with temperature, in particular for the case of high doping, indicates that the main contribution to the transport is strongly shifting to higher energies if the temperature increases. In order to make this observation more quantitative let us consider $V(T)$. The decrease of $V(T)$ for $T > T_0$, of course, must not be misinterpreted as a decrease of "activation energy" $V(T) + E_0 - \epsilon_F(T)$ (as it appears formally). Actually, $V(T)$ was only introduced in (7) as a form of writing the temperature dependence of the prefactor $\sigma_0(T)$, which was more appropriate for our analysis. The correct interpretation for the decrease of $V(T)$ at higher temperatures is consistent with increasing $W(T)$. Decreasing $V(T)$ corresponds to an increase of the prefactor $\sigma_0(T)$, which originates from the increasing contribution of carriers at higher energies where mobility $\mu(\epsilon)$ and density of states $N(\epsilon)$ are larger. We deduce

from $V(T)$ in Fig. 6 that $\sigma_0(T)$ increases, depending on the amount of doping, by about a factor of 15 to 40 within the temperature range of the experimental data. These results agree qualitatively with the predictions of the above-mentioned models which consider the transport as a sum of contributions from hopping in tail states and from band conduction above the mobility edge, the former one dominating at low, the latter one at high temperatures.

Our analysis, however, enables us to deduce more detailed information on the transport from the knowledge of $\sigma_0(T)$. In connection with the expression (19) we mentioned that $\sigma_0(\beta = (kT)^{-1})$ is the Laplace transform of the differential conductivity $\sigma(\epsilon) = e\mu(\epsilon)N(\epsilon)$. Now we can calculate the latter one by backtransformation. Fortunately, this task may be performed quite easily, since an analytical expression for $V(T)$ can be obtained from the experimental results on $W(T) - V(T)$, shown in Fig. 4. These curves may be approximated within experimental error by straight lines

$$W(T) - V(T) = nk(T - T_0) \tag{25}$$

with n ranging from about 7 to 9 and T_0 from 100 to 200 K. Using (11) one can integrate (25) with the results

$$V(T) - V(T_0) = nkT_0[\ln(T/T_0) + 1 - T/T_0] \tag{26}$$

and

$$W(T) - W(T_0) = nkT_0 \ln(T/T_0). \tag{27}$$

The $V(T)$ and the $W(T)$ curves in Fig. 6 have been obtained from (26) and (27) with the appropriate V_0, n, and T_0 values. The fit to the experimental data evidently is very good.

The Laplace backtransform, given by

$$\sigma(\epsilon) = (2\pi i)^{-1} \int_{-\infty}^{\infty} d\beta \, e^{\beta\epsilon} \sigma_{00} e^{-\beta V}$$

$$= \frac{e^n \sigma_{00}}{\pi k T_0} \int_0^{\infty} dx \exp(-n\pi x/2)$$

$$\times \cos[x(\tilde\epsilon + n\ln x - 1)] \tag{28}$$

with $x = \beta/\beta_0$ and $\tilde\epsilon = \beta_0(\epsilon - V_0)$, and computed numerically with the respective V_0, n, and T_0 values from above is shown in Fig. 7 for the whole set of samples (with exception of sample 1). We notice that $\sigma(\epsilon)$ shows a steep increase over several orders of magnitude within a range of about 200 meV before it tends to saturate at a value of about 10^4 $(\Omega\,\text{cm eV})^{-1}$. It is interesting to note that this value corresponds rather exactly to $\sigma(\epsilon)$ as deduced from Mott's expression for the minimum metallic conductivity[1]

$$\sigma_{\min} = 0.026 e^2/\hbar a \approx 200-300 \ (\Omega\,\text{cm})^{-1}. \tag{29}$$

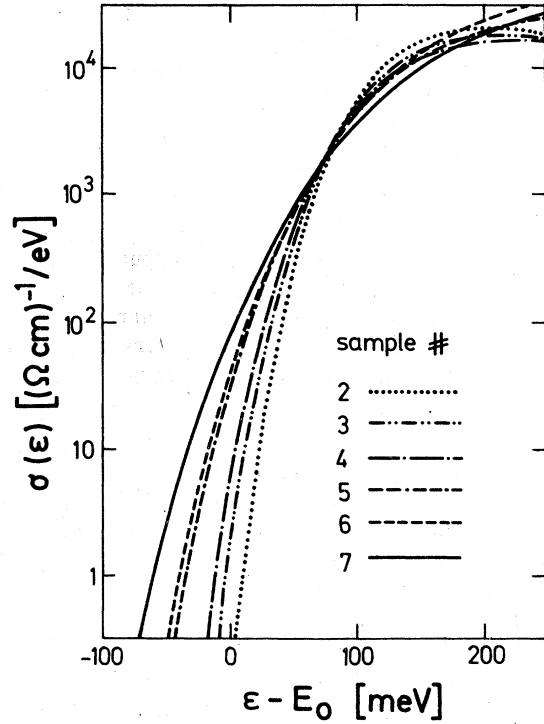$\sigma_{\min}$ and the differential conductivity at the mobility

FIG. 7. Differential conductivity $\sigma(\epsilon) = eN(\epsilon)\mu(\epsilon)$ obtained by Laplace backtransformation of $\sigma_0(\beta)$ with $V(T)$ from the analytical fit shown in Fig. 6.

edge $\sigma(\epsilon = E_c)$ are related to each other by the Kubo-Greenwood formula

$$\sigma_{\min} = \left(\int d\epsilon \, \sigma(\epsilon)[df(\epsilon - \epsilon_F)/d\beta\epsilon] \right)_{\epsilon_F = E_c}$$

$$\approx kT\sigma(E_c), \tag{30}$$

which yields

$$\sigma(E_c) = \sigma_{\min}/kT \approx (0.8 \text{ to } 1.2) \times 10^4 \ (\Omega\,\text{cm eV})^{-1} \tag{31}$$

at room temperature.

Another important observation concerns the region of lower energies in Fig. 7 in which $\sigma(\epsilon)$ decreases over say about 4 orders of magnitude. In spite of this strong drop it appears still reasonable to assume rather small phonon energies in the hopping processes between those localized tail states. This can be seen easily if we consider a diffusion-type expression for conduction in extended and localized states as well,[1,2]

$$\sigma(\epsilon) = N(\epsilon)e^2\gamma R^2/6kT. \tag{32}$$

R is the phase coherence length for extended states, and a mean hopping distance in the case of localized states. γ is assumed to be of the order of an electronic interatomic hopping frequency

$$\gamma^{\text{el}} \approx 10^{14} \text{ to } 10^{15} \text{ sec}^{-1} \tag{33}$$

for conduction in extended states.

With $N(E_c) \approx 10^{21}$ cm^{-3} eV^{-1}, e.g., a value of R ≈ 10–30 Å follows from σ_{min}. For hopping between localized states i and j, γ has the well-known form[7,15]

$$\gamma_{ij}^{\text{nop}} = \gamma_0^{\text{hop}} \exp(-\alpha R_{ij} - \beta \mid \epsilon_{ij} \mid). \qquad (34)$$

If $N(\epsilon)$ decreases by a factor 10 within the energy range considered, it follows that γR^2 should decrease by a factor $10^{-3} \approx e^{-7}$. There is some controversy about the magnitude of γ_0.[7,16] It seems reasonable, however, that $\gamma_0^{\text{hop}} \langle R_{\text{nearest neighbor}}^{\text{hop}} \rangle_{av}^2$ at least should not be larger than $\gamma^{el} R_{el}^2$. Thus an exponent of -7 in (34) is sufficient. It follows that the average phonon energy for hopping is less than $2kT$, even at the lowest energies considered, since $\beta \mid \epsilon_{ij} \mid$ on the average contributes only $\frac{1}{4}$ to this exponent in a random distribution of localized states.[7] Similarly one can see that the average value of the exponent does not change drastically with temperature in the range $T = 200$–600 K. The former observation shows that our use of the Kubo-Greenwood expressions (4) and (8) for the transport quantities was allowed, the latter one justifies our approximation introduced by neglecting the temperature dependence of $\mu(\epsilon)$.

It is instructive to visualize how the different energies contribute to $\sigma_0(T)$ at different temperatures. As an example the integrand $\sigma(\epsilon) \exp[-\beta(\epsilon - E_0)]$ from (19) is shown in Fig. 8 together with the corresponding values of $W(T) - E_0$ for some temperatures for sample number 7.

Though the results on $\mu(\epsilon)$ for the different samples resemble each other qualitatively, Fig. 7 reveals a clear tendency that the decrease of $\sigma(\epsilon)$ becomes less steep with increasing amount of doping. This observation can be interpreted as the effect of enhanced hopping mobility due to additional localized states in this energy range introduced by the substitutional doping. One might speculate whether the decrease of $\sigma(\epsilon)$ which appears at higher energies is due to an erosion of the density of states in this range as a result of conservation of the total number of states. However, one should be cautious, bearing in mind, that the Laplace transform involves contributions from energies for which our analytical fit to the experimental data possibly no longer represents adequately the real physical situation.

Finally a few remarks concerning the statistical shift should be made. We have learned from our analysis that the temperature dependence of W increases with increasing amount of doping (see Fig. 6). As a consequence we deduce a statistical shift $\epsilon_F(T)$, which is less pronounced at high and more pronounced at low doping level in comparison with the corresponding shifts, shown in Fig. 4, in the
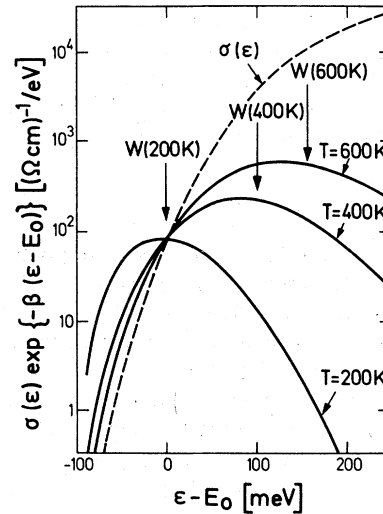

FIG. 8. Differential contribution to σ_0 (T) at the energy ϵ for sample 7. The distribution function broadens and shifts to higher energies with increasing temperature. The peak is close to $W(T) + E_0$, as indicated by the arrows.

work by Beyer et $al.$[4] We recall that the latter analysis was based on an ad hoc model for a reasonable $W(T)$, which was assumed as doping independent, in contrast to our $W(T)$ directly determined from experiment.

Of course, it would be an interesting test to compare the results on $\epsilon_F(T)$ for the various samples with the statistical shift calculated from $N(\epsilon)$ according to Eq. (2), provided that reliable information on $N(\epsilon)$ from field effect[13] or C vs U measurements[14] exists. Such a comparison, in particular, could provide evidence on whether the neglect of the temperature dependence of the differential mobility $d\mu(\epsilon)/dT$, indeed, is justified.

In our discussion following expression (18) we mentioned that the difference $X(T)$ [defined by (12)] between the true statistical shift and our result should be a doping-independent quantity according to our initial assumptions. Although we found that $N(\epsilon)\mu(\epsilon)$ actually does change with doping, we still expect that $X(T)$ should show a qualitatively similar behavior at different doping levels. Indeed, we note that all our $\epsilon_F(T)$ curves (see Fig. 6) flatten at higher temperatures, in contrast to $\epsilon_F(T)$ as calculated from simple models for $N(\epsilon)$. Beyer et $al.$[4] postulated a doping-dependent peak density of states below ϵ_F in the $N(\epsilon)$ curve in order to obtain agreement between calculated and experimental $\epsilon_F(T)$ curves. As an alternative one might speculate whether the apparent flattening, which is common to the results at all the doping levels, should be attributed to the neglect of the temperature dependence of $\mu(\epsilon)$ and the resulting neglect

of the term $X(T)$ from (12) on the right-hand side of (15) and in the integration in (16).

The quantities which determine $X(T)$ are known from our analysis except for $d\ln\mu(\epsilon)/dT$. Actually, from (12) we see that $X(T)$ can be interpreted as an average

$$X(T) = kT^2 \langle d\ln\mu(\epsilon)/dT \rangle . \tag{35}$$

The weighting function in the averaging procedure is just the expression $N(\epsilon)\mu(\epsilon)\exp[-\beta(\epsilon - E_0)]$ already shown in Fig. 8 for different temperatures.

According to the expected qualitative behavior of $d\mu(\epsilon)/dT$ as indicated in Fig. 2 we should find that $X(T)$ is positive at low temperatures when hopping dominates since increasing temperature stimulates the hopping mobility. $X(T)$ should decrease at higher T and finally change sign if the main contribution to (30) comes from energies above E_c, since increasing temperature lowers the mobility for conduction in extended states.

The apparent flattening of our $\epsilon_F(T)$ curves in Fig. 5 would correspond to positive $X(T)$ at high temperatures, and it may be interpreted as an indication that hopping still dominates the transport even at temperatures of the order of 600 K, provided that the flattening is not due to some peculia-

rities in the density-of-states distribution. A decision on this point can be made only once the accurate shape of $N(\epsilon)$ is known.

The purpose of this paper, however, was not an unambiguous interpretation of experimental data, but rather we intended to show that our analysis provides a lot of new information and may help to a better understanding of the transport properties of amorphous semiconductors and of the influence of doping.

In conclusion we would like to point out three major results. First, we were able to deduce the energy-dependent differential conductivity $\mu(\epsilon)$ for an amorphous semiconductor. Second, we have found that the density-of-states distribution $N(\epsilon)$ and/or the mobility $\mu(\epsilon)$ change appreciably with doping. Third, there are indications that the dominant transport mechanism in amorphous silicon is always hopping below the mobility edge, even in glow-discharge samples and at temperatures close to the recrystallization point.

ACKNOWLEDGMENTS

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energy not too far below the mobility edge and at relatively high temperatures as considered in this work.

[11]Kubo-Greenwood formulas, similar to our expressions (4) and (8) were also used in the work by Friedman[5] as starting point. His anlysis, however, is closer in its spirit to Refs. 3, 4, and 6, since model assumptions for the shape of $\mu(\epsilon)$ are made also in his model, whereas no such assumptions are necessary in our combined analysis of conductivity plus thermopower data.

[12]A careful discussion of $\mu(\epsilon, T)$ would require a distinction between Mott's[1] and Cohen's[2] picture concerning the behavior of $\mu(\epsilon, T = 0)$ at the mobility edge E_c.

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