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Low Temperature Polaronic Hopping Conduction

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The dc-hopping conductivity and thermopower is calculated for temperatures below half the Debye temperature θ_D. A percolation approach with multiphonon hoprates is used. Two sets of energetically overlapping states near the Fermi level are considered. The coupling to the phonons is assumed to be larger for the lower lying set of states. The resulting thermopower is negative and slowly varying with temperature, but bends down to higher negative values at low ($\approx 0.1\theta_D$) temperatures. The conductivity essentially follows a $\ln \sigma \sim T^{-1/4}$ law. The thermopower is much more stable with respect to changes in the density of states as compared to a model without multiphonon effects.

Die Gleichstromleitfähigkeit und Thermokraft werden für Temperaturen unterhalb der halben Debye-Temperatur θ_D im Rahmen der Perkolationstheorie unter Berücksichtigung von Multiphononen-Hopraten berechnet. Es werden zwei Gruppen von Zuständen angenommen, die sich energetisch in der Nähe des Fermi-Niveaus überlappen. Die tieferliegende Gruppe ist stärker an die Phononen gekoppelt. Es ergibt sich eine schwach temperaturabhängige negative Thermokraft, die bei tiefen Temperaturen ($\approx 0{,}1\theta_D$) nach größeren negativen Werten hin abknickt. Die Leitfähigkeit folgt im wesentlichen einem $\ln \sigma \sim T^{-1/4}$-Verhalten. Die Thermokraft reagiert sehr viel schwächer auf Änderungen in der Zustandsdichte als in einem Modell ohne Multiphononen-Effekte.

1. Introduction

A large amount of transport data for amorphous germanium and silicon has been accumulated in the literature. It is widely believed that for low temperatures they can be interpreted in terms of Mott's variable range hopping model [1]. It can be stated, however, that a number of generally observed features has not been satisfactorily explained.

Let us first consider the dc conductivity. It can usually be nicely fitted to Mott's formula

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right]. \tag{1}$$

For a constant density of states N_F at the Fermi level E_F, Mott obtains

$$T_0 \approx 18.1\,(\alpha^3 k N_F)^{-1}\,, \tag{2}$$

where α is the decay length of the localized wave functions and k the Boltzmann constant. This model provides us with a number of well-known problems. Here we are concerned with the following:

(i) Assuming that the density of states decreases upon annealing, T_0 should increase as N_F^{-1}. However, it is usually found that T_0 is rather insensitive to annealing and sample preparation [2], i.e. to the density of states.

(ii) Spin resonance measurements on evaporated and sputtered samples yield a density of unpaired spins (10^{19} to 10^{20} /cm^3) [3] which is much larger than the number of states deduced from (2), inserting the experimentally observed T_0 [4]. Taking a typical (a-Si) $T_0 = 1.8 \times 10^8$ K, $\alpha = 5$ Å, and a band width of 0.5 eV, we get $4 \times 10^{18}/\text{cm}^3$ spins provided that all these states are associated with an unpaired spin.

Of course the constant density-of-states model has to be abandoned. Starting from hop rates [5, 6] (including electron statistics)

$$\Gamma_{ij} \sim \exp\left(-\frac{2r}{\alpha} - \frac{E_{ij}}{kT}\right); \tag{3}$$

$$E_{ij} = \frac{1}{2}\left(|E_i| + |E_j| + |E_i - E_j|\right).$$

Overhof and Thomas [7] have used a percolation approach [8] to calculate σ. (Here r is the hopping distance, E_i and E_j are the localized state energies.) For a special set of density-of-states functions, $N(E)$, a parallel shift of the $\ln \sigma$ versus $T^{-1/4}$ curves results as the number of states is decreased. To these density-of-states functions a number of spins would correspond, which is considerably larger than that calculated with a constant N_F.

This approach is based on hop rates which have not been proved to apply in the situation of hopping in amorphous semiconductors. Rather multiphonon hoprates have to be considered. Emin [9] has shown that the multiphonon hoprate has itself a temperature dependence not unlike equation (1). However, in order to obtain T_0 from multiphonon hoprates in the region of experimental values, one has to allow for rather high (8 to $10\hbar\omega_D$) polaronic binding energies [10]. With Debye energies $\hbar\omega_D$ of 5.6×10^{-2} and 3.2×10^{-2} eV for a-Si and a-Ge, respectively, this implies binding energies which in Si are nearly as large as half the gap. This is hard to understand if we assume, as is usually done, the localized states to derive from structural defects. So one has to conclude that the experimentally observed T_0 is at least partly due to statistics, i.e. to percolation effects in the variable range hopping model.

The dc conductivity alone does not seem to be a suitable means to test theoretical models. One should rather calculate the thermopower S and compare it to experimental data. Here the interpretation is also not yet clear. For our purpose let us consider the following problems:

(i) In the majority of cases a small negative value of the thermopower is found at low temperatures, varying slowly with T [11, 12]. In the hopping model the sign of S is given by the sign of $-\left((\mathrm{d}/\mathrm{d}E)\,(N(E))\right)|_{E=E_F}$. It is then hard to understand why usually the density-of-states function $N(E)$ has a positive slope at E_F. We may state that S is much more insensitive with respect to changes of $N(E)$ than a percolation approach with hoprates (3) would predict.

(ii) For very low temperatures Lewis [11] reports a new behaviour of S in a-Ge. With decreasing T, S first is negative and nearly constant; at $T \approx 0.1\,\theta_D$ (θ_D Debye temperature) it bends down to larger negative values. Lewis based his interpretation on transport in a very narrow band (0.01 eV). This assumption seems to be rather artificial for amorphous semiconductors.

For a better understanding of the above-mentioned problems we extend the percolation approach of Overhof [13] by using multiphonon hoprates. We calculate σ and S in the temperature range $0.1\theta_D \lessapprox T \lessapprox 0.5\theta_D$. We assume a density-of-states function similar to that employed in [7], which is composed of two sets of states which have different strengths of coupling to the phonons. Within this model we are able to understand the behaviour of S in Lewis' experiments. This model also explains the reduced sensitivity of S to changes in $N(E)$ in a large temperature interval.

2. The Multiphonon Hoprate

We calculate the multiphonon hoprate starting from Emin's [9] expression. To facilitate the numerical effort, the calculations are done in frequency space [10] (see Appendix). Using exponential electronic wave functions, $\alpha = a$ (lattice constant $a \approx 5$ Å), and $r = 10a$, we obtain hoprates ν which are depicted in Fig. 1 for a binding energy $E_\text{b} = 5\hbar\omega_\text{D}$. The binding energy in this case is given approximately by

$$E_\text{b} \approx \frac{\gamma}{6V}\,\hbar\omega_\text{D}\;; \qquad V = \frac{4\pi}{3}\,\alpha^3\;, \tag{4}$$

where γ characterizes the strength of the electron–phonon coupling.

In analogy to (3) we write, including electron statistics;

$$\Gamma_{ij} = \Gamma_0 \exp\left[-\frac{2r}{\alpha} - \frac{E_{ij}}{kT} - \frac{W(\Delta, T, E_\text{b})}{kT}\right]; \qquad \Delta = E_i - E_j\,. \tag{5}$$

Since we are interested here in low temperatures, we approximate $E_{ij} + W(\Delta, T, E_\text{b})$ by the slope of $\ln \nu$ versus T^{-1} at $T = 0.1\theta_\text{D}$ in Fig. 1:

$$E_{ij} + W(\Delta, T, E_\text{b}) \approx E_{ij} + W_{E_\text{b}}(\Delta)\,. \tag{6}$$

From equations (A 1) to (A 4) we see that

$$W_{E_\text{b}}(\Delta) = W_{E_\text{b}}(|\Delta|)\,. \tag{7}$$

For simplicity we write

$$W_{E_\text{b}}(|\Delta|) = W_{E_\text{b}}(0)\,f(|\Delta|)\,; \qquad f(0) = 1\,. \tag{8}$$

In Fig. 2 the dependence of $W_{E_\text{b}}(0)$ on E_b is shown. The dependence of W on Δ is depicted in Fig. 3 for two binding energies $5\hbar\omega_\text{D}$ and $2\hbar\omega_\text{D}$. W serves as an additional activation energy, which is largest for hops between sites of equal energy and decreases rapidly with increasing energy separation. This will be shown to yield interesting results for the thermopower at low temperatures.

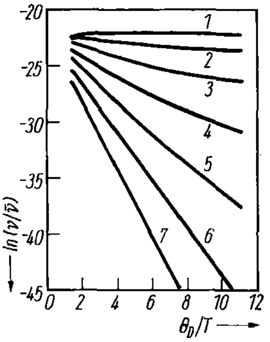

Fig. 1

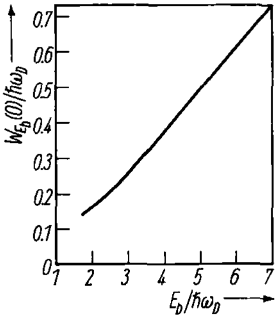

Fig. 2

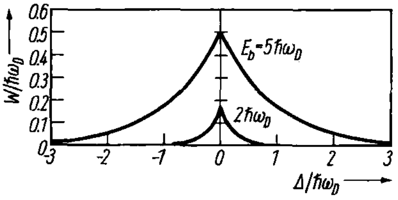

Fig. 3

Fig. 1. Multiphonon hoprate as a function of T^{-1} for different energy separations Δ. $E_\text{b} = 5\hbar\omega_\text{D}$, $\alpha = a$, $R = 10a$. (1) $\Delta = -3$, (2) -2, (3) -1, (4) 0, (5) 1, (6) 2, (7) $3\hbar\omega_\text{D}$

Fig. 2. Dependence of $W_{E_\text{b}}(0)$ on E_b taken from the slope of Fig. 1 at $T = 0.1\theta_\text{D}$

Fig. 3. Dependence of W on energy separation Δ for $E_\text{b} = 5\hbar\omega_\text{D}$ and $E_\text{b} = 2\hbar\omega_\text{D}$

3. The Model for the Localized States

A large body of experimental data for evaporated and sputtered a-Ge and a-Si can be interpreted assuming a double-peaked density-of-states function $N(E) = N_1(E) + N_2(E)$, E_F being somewhere in the region of overlap of the two peaks [7, 12, 14]. Spin density is usually rather high in these samples [3]. This suggests that the set of states peaked at a lower energy ($N_1(E)$) is due to singly occupied states, the set peaked at a higher energy due to doubly occupied states of some defects. They are separated by a positive intrasite correlation energy, and

$$\int N_1(E)\,\mathrm{d}E = \int N_2(E)\,\mathrm{d}E\,. \tag{9}$$

Then it is natural to assume that the doubly occupied ($N_2(E)$) states have a larger α and due to (4) smaller binding energies than the singly occupied states.

To be consistent one also has to consider the different α in the tunneling factor $\exp(-2r/\alpha)$. But since W is proportional to α^{-3}, we can neglect the variation of the tunneling factor, always setting α equal to one lattice constant there.

This model, however, is not a necessary ingredient of our theory. Any other model, where a lower lying set of states having a larger coupling to the phonons overlaps with a higher set of states, could be included into the calculation yielding the same answers for σ and S.

Since we are now considering two sets of states having different binding energies, we can no longer deal with only a single $W_{E_\mathrm{b}}(\Delta)$. As a reasonable ansatz we take the generalized $W_{ij}(\Delta)$ to be

$$\begin{aligned} W_{ij}(\Delta) &= W_{0ij}\, f(|\Delta|)\,; \\ W_{0ij} &= \tfrac{1}{2}[N_1(E_i)\, W_{E_{\mathrm{b},1}}(0) + N_2(E_j)\, W_{E_{\mathrm{b},2}}(0) + \\ &\quad + N_1(E_j)\, W_{E_{\mathrm{b},1}}(0) + N_2(E_j)\, W_{E_{\mathrm{b},2}}(0)], \end{aligned} \tag{10}$$

where $W_{E_{\mathrm{b},1}}(0)$ and $W_{E_{\mathrm{b},2}}(0)$ are given by the binding energies of the lower and higher states, respectively, according to Fig. 2.

4. The Calculation of σ and S

We use Overhof's method [13] to calculate first the critical exponent ξ, from which we then obtain σ and S. Introducing the equivalent resistor network [5], then in the framework of percolation theory all conductances on a critical path are smaller than $\exp(-\xi)$. The critical path is formed if on the average a site has μ bonds, i.e., μ hops are possible away from an average site with $\Gamma > \exp(-\xi)$. We take μ to be 2.6 [13]. The number of bonds of a given site i is

$$n(E_i\,\zeta) = \frac{4\pi}{3}\left(\frac{\alpha}{2kT}\right)^3 \int (\zeta - E_{ij} - W_{ij})^3\, N(E_j)\,\mathrm{d}E_j\,, \tag{11}$$

where $\zeta = \xi\, kT$ is the critical energy, which may be obtained by solving

$$\mu = \frac{\int n^2(E_i, \zeta)\, N(E_i)\,\mathrm{d}E_i}{\int n(E_i, \zeta)\, N(E_i)\,\mathrm{d}E_i} \tag{12}$$

for a given temperature. It is easier, however, to calculate the temperature T for a given ζ, since T appears only in the prefactors of the integrals. Once having determined T for a given ζ, we have immediately

$$\frac{\sigma}{\sigma_0} = \exp\left(-\frac{\zeta}{kT}\right) \tag{13}$$

and S can be calculated by Overhof's equations (6) to (12) [13].

5. Results

In Fig. 4 we show the model for the density-of-states functions used. The density-of-states at the Fermi level (near its minimum) is $8.5 \times 10^{18}/\text{eV cm}^3$ and $1.3 \times 10^{18}/\text{eV cm}^3$ for Si and Ge, respectively. Except at the lowest temperatures, the hopping conductivity follows equation (1) (Fig. 5), T_0 being $\approx 7.0 \times 10^5\ \theta_D$ (4.5×10^8 K for Si, 2.6×10^8 K for Ge). For a symmetric $N(E)$ and a uniform binding energy for all states we get $S \equiv 0$. If E_b is larger for the lower set of states than for the higher set, S is negative and $|S|$ increases for decreasing T (Fig. 6). This reflects the fact that for decreasing temperatures, states belonging to the set with higher binding energy are frozen out and do not contribute to the transport. So, if T is low enough, only the higher peak in $N(E)$ is effective with a large positive slope at the Fermi level (thin line in Fig. 4).

On the other hand, for symmetric E_b but asymmetric $N(E)$, $|S| \sim T^{1/2}$ for $T \to 0$, the sign being determined by the sign of $-(\mathrm{d}/\mathrm{d}E)\,(N(E))|_{E=E_F}$. If both E_b and $N(E)$ are asymmetric, we get a superposition of both effects, i.e., S is slowly varying for higher T, but bends down at a given characteristic temperature. It is interesting to note that the conductivity gradually deviates from the familiar $T^{-1/4}$ behaviour at the lowest temperatures.

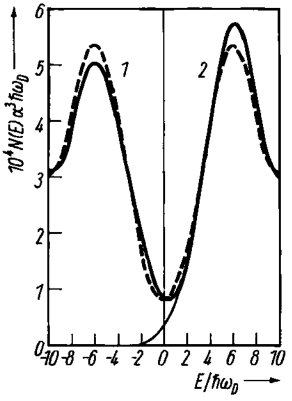

Fig. 4

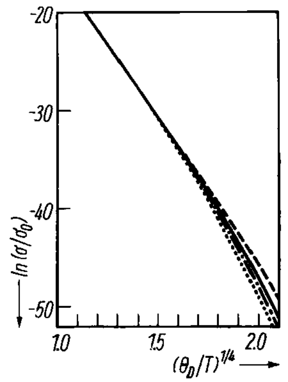

Fig. 5

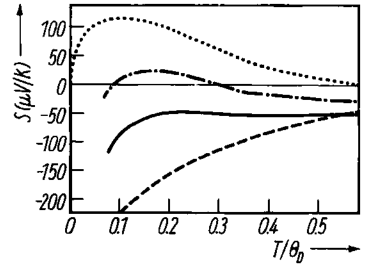

Fig. 6

Fig. 4. Symmetrical (dashed curve) and asymmetrical (solid curve) density of states. At low temperatures only the higher set of states 2 is effective, which has a large slope at $E = E_F = 0$ (thin)

Fig. 5. Hopping conductivity versus $T^{-1/4}$ for: $W_{E_{b,1}} = 0.7\hbar\omega_D$, $W_{E_{b,2}} = 0.1\hbar\omega_D$, $N(E)$ symmetric (dashed curve); $W_{E_{b,1}} = 0.7\hbar\omega_D = W_{E_{b,2}}$, $N(E)$ asymmetric (dotted curve); $W_{E_{b,1}} = 0.7\hbar\omega_D$, $W_{E_{b,2}} = 0.1\hbar\omega_D$, $N(E)$ asymmetric (solid curve); $W_{E_{b,1}} = 0.7\hbar\omega_D$, $W_{E_{b,2}} = 0.35\hbar\omega_D$, $N(E)$ asymmetric (dash-dotted curve)

Fig. 6. Thermopower results versus T. Symbols as in Fig. 5

In the light of our model, the result of Lewis can be easily understood. Assuming binding energies $7\hbar\omega_D = 0.22$ eV and $1\hbar\omega_D = 0.03$ eV for the higher and lower set of states, a behaviour can be obtained that is quite similar to that found by Lewis of a-Ge (solid line in Fig. 6). His a-Si results can be understood either by assuming a smaller asymmetry in the binding energies, or a larger asymmetry of $N(E)$ (dashed-dotted line in Fig. 6). (Here we did not attempt to fit the experimental data quantitatively. This could easily be done using different $N(E)$ functions for Ge and Si.)

To reproduce Lewis' results within our model it is essential to consider two sets of states which overlap near the Fermi level, and to make the natural assumption that the lower lying set of states is more strongly coupled to the phonons than the higher one. (If the states below E_F are associated with an unpaired spin, then there should be a spin density of the order of several $10^{19}\,\text{cm}^{-3}$ in our model.) The asymmetry of the electron–phonon coupling leads to a negative S. If this asymmetry is large enough, S is negative down to the lowest temperatures. This effect is rather insensitive to the form of $N(E)$. With decreasing temperature, S is first slowly varying with T. At a given low T, which depends on the degree of asymmetry in the coupling, S rapidly goes to larger negative values. The sharpness of this kink is determined by the slope of the contribution to $N(E)$ from the higher set of states.

Our model is based on electron–phonon interaction with only acoustic phonons. As Gorham-Bergeron and Emin [15] have demonstrated, the additional coupling to the optical phonons does not lead to qualitatively different results for the hoprate, as long as the coupling to acoustic phonons is not much weaker than to optical phonons.

Acknowledgement

We would like to thank Prof. H. Overhof for helpful discussions.

Appendix

Let us consider an electron hopping from a localized state to another one, separated by a distance r and an energy $\Delta = \hbar\Omega$, interacting with acoustic phonons (Debye model: $0 \leqq \omega = vq \leqq \omega_D$) via a deformation potential interaction characterized by a strength γ. Then the multiphonon hoprate [9] can be calculated easily using the formula [10]

$$\nu = \bar{\nu}\omega_D\, e^{-2r/\alpha}\, e^{-\hbar\Omega/2kT}\, e^{-2\Sigma} \sum_n \frac{1}{n!}\, r_n(\Omega) \ . \tag{A 1}$$

The n-phonon contribution ($n > 1$) is given by the convolution

$$r_n(\Omega) = \int_{-\omega_D}^{\omega_D} d\omega\, r_1(\omega)\, r_{n-1}(\Omega - \omega) \tag{A 2}$$

and $r_1(\omega)$ is the interaction function

$$r_1(\omega) = \frac{3}{2}\,\gamma\,\frac{\omega}{\omega_D}\left[1 - \frac{\sin\,(\omega r/v)}{(\omega r/v)}\right] \Phi^2\left(\frac{\omega}{v}\right) \operatorname{cosech}\left(\frac{h\omega}{2kT}\right). \tag{A 3}$$

v is the velocity of sound, $\bar{\nu} = 2\pi\omega_D\,(I_0/\hbar\omega_D)^2$, I_0 is the electronic transfer integral, and

$$\Phi(q) = \int e^{i\boldsymbol{q}\boldsymbol{r}}\, |\varphi(\boldsymbol{r})|^2\, d^3r \tag{A 4}$$

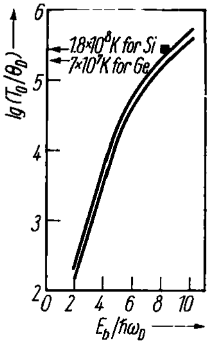

Fig. 7. T_0 as a function of E_{b}. ■ Emin's [9] result. Higher curve Lorentzian, lower curve exponential $\varphi(\boldsymbol{r})$

$\exp(-2\,\Sigma)$ is the band-narrowing factor with

$$2\Sigma = \int\limits_{-\omega_{\mathrm{D}}}^{\omega_{\mathrm{D}}} \mathrm{d}\omega\, r_1(\omega) \cosh\left(\frac{\hbar\omega}{2kT}\right). \tag{A 5}$$

For $r > 5a$ (a is the lattice constant) the dependence of ν on r is mainly through the factor $\exp(-\,2r/\alpha)$, and the coherence factor $1 - \sin(\omega r/v)/(\omega r/v)$ in (A 3) can well be approximated by unity. Since we do not know the magnitude of γ and α, we use the polaronic binding energy

$$E_{\mathrm{b}} = \frac{3\gamma\hbar}{\omega_{\mathrm{D}}^2} \int\limits_0^{\omega_{\mathrm{D}}} \mathrm{d}\omega\, \omega^2 \Phi^2\left(\frac{\omega}{v}\right) \tag{A 6}$$

as the physical parameter determining the strength of the interaction. For simplicity α is set equal to one lattice constant a (≈ 5 Å). The electronic wave function $\varphi(\boldsymbol{r})$ enters the hoprate via a convolution of the Fourier-transformed $|\varphi(\boldsymbol{r})|^2$. So it is clear that the details of $\varphi(\boldsymbol{r})$ do not influence the hoprate significantly. To test the influence of $\varphi(\boldsymbol{r})$ we have calculated ν for exponential as well as Lorentzian wave functions [16]. We also have replaced $r_1(\omega)$ by the interaction function used by Emin [9], which assumes full strength of the interaction for phonons with frequencies up to $0.5\hbar\omega_{\mathrm{D}}$, and no interaction for larger ω.

In Fig. 1 we show ν versus T^{-1} for $E_{\mathrm{b}} = 5\hbar\omega_{\mathrm{D}}$ and $r = 10a$. ν deviates from a $\nu \approx \exp(-\Delta/kT)$ behaviour for $T \gtrsim 0.1\theta_{\mathrm{D}}$; it approaches this activated behaviour for larger Δ and/or lower T. When the $\Delta = 0$ data are plotted versus $T^{-1/4}$, we can extract an effective T_0 (valid for $0.1\theta_{\mathrm{D}} \lesssim T \lesssim 0.5_{\mathrm{D}}\theta$). These are plotted in Fig. 7 as a function of E_{b} for Lorentzian and exponential $\varphi(\boldsymbol{r})$, and for Emin's interaction function. There we have also indicated typical experimental T_0 for a-Ge and a-Si. Since the T_0 versus E_{b} relation seems to be rather insensitive to the specific models employed for the interaction function, we conclude that the experimentally observed T_0 is not due to polaronic effects alone. (The inclusion of additional coupling to optical phonons by Gorham-Bergeron and Emin [15] does fit in with our results. Their data, however, fall outside the range of the binding energies considered here.)

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