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Numerical approach to hopping conduction

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A numerical method for calculation of the polarization conductivity has been developed. This approach has been applied to the correlated barrier hopping (CBH) and quantum mechanical tunnelling (QMT) models in the case of monoelectronic hops. These calculations have been performed on well-known solids such as carbon (HTT 600° C) and badly organized molybdenum and tungsten sulphides. The agreement between theory and experimental results is more satisfying than in a previous approach. The parameters W_M and N_0 are determined for the CBH model, and $N(E_F)$ for the QMT model.

1. Introduction

Following Anderson's work [1] on the concept of localized states in amorphous or badly organized compounds, Miller and Abrahams [2] developed the study of the transfer of charge carriers between these states. Since then, a set of models has been devised to describe, particularly, the evolution of conduction as a function of frequency [3–8]. In most cases the $\sigma_{\text{a.c.}}$ values measured are considered as being the sum of the two following terms

$$\sigma_{\text{a.c.}} = \sigma'(\omega) + \sigma_{\text{d.c.}} \qquad (1)$$

$\sigma'(\omega)$ is the real part of the polarization conductivity caused by electron movement under the effect of an alternating electrical field with a circular frequency ω. $\sigma_{\text{d.c.}}$ is the conductivity for direct current.

The behaviour of the experimental results is generally described by a law with the following form

$$\sigma'(\omega) = A(T)\omega^s \qquad (2)$$

It is therefore possible to determine parameters $A(T)$ and s experimentally.

This type of variation is usually associated with the displacement of carriers which move within the sample by discrete hops of length R between randomly distributed localized sites. Analysis of polarization moments associated with this movement leads to [6, 8]

$$\sigma'(\omega) = \frac{N^2}{2}\int_{R_0}^{R_\infty} \alpha(R)p(R)\frac{\omega^2\tau}{1+\omega^2\tau^2}\,\mathrm{d}R \qquad (3)$$

where N is the number of sites per unit volume, $\alpha(R)$ is the polarizability. Pollak and Geballe [9] proposed that the following expression should be chosen for α

$$\alpha(R) = \frac{e^2R^2}{12kT} \qquad (4)$$

Starting from a site, $p(R)$ is the probability of another site being located at a distance between R and $R + \mathrm{d}R$.

Finally, τ is the relaxation time associated with a hop of distance R. An Equation associating τ with R is required in order to continue the calculation using Equation 3. It is possible to relate these quantities by using hypotheses concerning the way in which carriers cross the potential barrier between two sites.

Two possibilities can be envisaged: either tunnelling or thermal activation. In both cases, the relationship between τ and R can be used to calculate the integral of Equation 3 as a function of a single parameter.

2. Calculation method

We attempted to maintain τ as a single parameter throughout the study. Integration limits are, therefore, τ (lower) and τ_∞ (upper). $\tau_0 = 1/\nu_0$ where ν_0 is the vibration frequency of the particle trapped at its site [3, 4]. τ_∞ is determined by calculation and is the value for which the integral is convergent. In this case we chose a text to guarantee a relative accuracy of 0.01% of the calculated value of $\sigma'(\omega)$.

The work described mainly differs from previous studies in the integration method used. It was decided to carry out numerical calculation of the value of the integral for which there is no analytical solution. As far as we know, this integration has always been carried out using approximations justified, of course, but the influence of which on the numerical results is not always specified. Thus, for example, it is generally assumed that

$$\text{integral} = \int_{(\omega\tau)_0}^{(\omega\tau)_\infty} \frac{\mathrm{d}(\omega\tau)}{1+\omega^2\tau^2} = \frac{\pi}{2} \qquad (5)$$

However, this value is only correct if $\omega\tau$ is sufficiently high, i.e. for high frequencies, or for large values of τ, physically unacceptable. Thus, $I = \pi/4$ is found when values are limited to $\tau = 10^{-2}$ sec, and $\omega = 100$ Hz. This means that I is not independent of ω in the range of the most accessible τ. This observation justifies the use of numerical methods to calculate the real part of polarization conductivity.

3. Experimental results

Conductivity was measured as a function of frequency in various amorphous compounds. We considered that the set of samples examined was satisfactorily representative of some of the different types of compounds encountered in the field of badly organized materials. Our experiments were thus carried out on the following samples:

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(i) anthracene coke, the highest treatment temperature (HTT) of which was 600° C [10];

(ii) amorphous molybdenum sulphide treated at 195° C, composition was such that S : Mo = 3.0 [11];

(iii) two other molybdenum sulphides treated at higher temperatures (500 and 700° C), the composition was characterized by an S : Mo ratio of 2.0. They were nevertheless distinct, particularly with regard to the degree of crystallinity [11];

(iv) finally, three tungsten sulphides prepared at temperatures lower than 300° C [12].

In all these samples, the conductivity $\sigma_{\mathrm{a.c.}}$ measured as a function of frequency obeyed the laws given in Equations 1 and 2 (see Figs 1, 2, 5 and 6). However, the behaviour of the parameter s varied and the samples can be divided into two groups in this respect:

1. s is independent of temperature for carbon samples with HTT = 600° C and molybdenum trisulphide (TT 195° C).
2. s varies as a function of temperature in all the other samples.

4. Interpretation

Hopping conduction models lead to two forms of behaviour of s as a function of T. When the values of s depend on T, the models generally used assume that the crossing of the potential barrier between two sites is thermally activated. These models are generally associated with the mechanism described by the term correlated barrier hopping (CBH). When s is independent of T, this behaviour is associated with tunnelling described by the quantum mechanical tunnelling model (QMT).

4.1. Use of the CBH model

This model was developed by Elliott [13], and is based on the following three basic hypotheses.

1. Electron hopping is caused by thermally activated crossing of the potential barrier W separating two sites. Pollak and Pike [14] demonstrated that the relaxation time associated with this mechanism takes the form

$$\tau = \tau_0 \exp(W/kT) \qquad (6)$$

where τ_0 has already been defined.

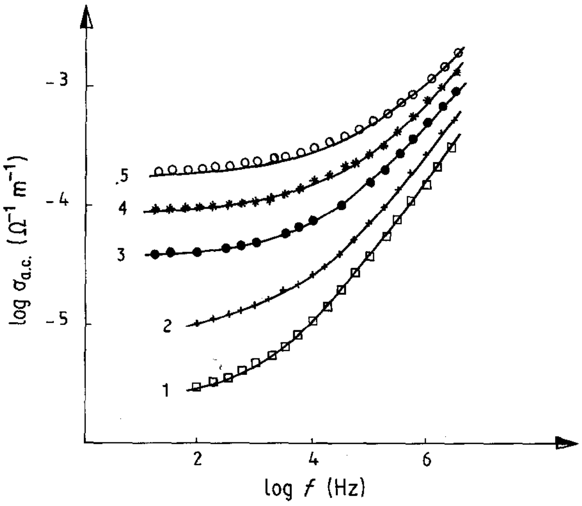

Figure 1 A.c. conductivity of MoS_2 (TT 700° C). Comparison between theory (CBH model solid lines) and experimental results. (1, T = 208 K; 2, T = 225 K; 3, T = 242 K; 4, T = 257 K; 5, T = 273 K.)

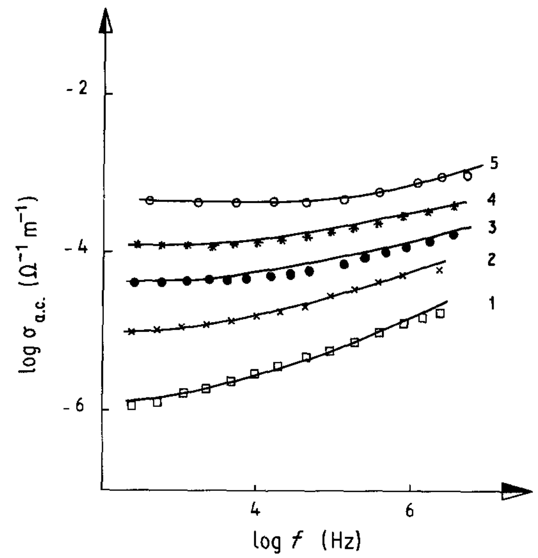

Figure 2 A.c. conductivity of a tungsten sulphide (example of $WS_{2.6}$). The solid lines are calculated using the CBH model. (1, T = 265 K; 2, T = 323 K; 3, T = 359 K; 4, T = 388 K; 5, T = 428 K.)

2. The height W of the potential barrier is related to the distance R between two sites, assuming that coulombic interactions are predominant [15, 16]

$$W_M - W = \frac{4e^2}{\varepsilon_s R} \qquad (7)$$

where W_M is the energy required to transport an electron from infinity to a site; ε_s can be considered as the static dielectric constant of the material.

3. The probability of finding a site at distance R from another site is homogeneous and isotropic, giving

$$p(R)\mathrm{d}R = 4\pi R^2 \mathrm{d}R \qquad (8)$$

The use of the three basic hypotheses gives

$$\sigma'(\omega) = \frac{\pi N^2}{24}\varepsilon_s\omega \int_{\tau_0}^{\tau_\infty} R^6 \frac{\omega}{1+\omega^2\tau^2}\,\mathrm{d}\tau \qquad (9)$$

Unlike the methods used previously [3–8], at this stage of calculation, R is expressed as a function of τ, τ_0 and W_M

$$R = \frac{4e^2}{\varepsilon_S W_M}\left[1 - \frac{kT}{W_M}\ln\left(\frac{\tau}{\tau_0}\right)\right]^{-1} \qquad (10)$$

TABLE I Values of W_M and the number of sites N as a function of the composition of the sulphides (CHB) model)

Compound	TT(° C)	W_M(eV)	N(cm^{-3})
$WS_{2.8}$	200	0.57	2.2×10^{18}
$WS_{2.6}$	230	0.54	2×10^{18}
$WS_{2.5}$	260	0.52	2×10^{18}
$MoS_{2.2}$	500	0.60	1×10^{18}
MoS_2	700	0.67	7.8×10^{16}

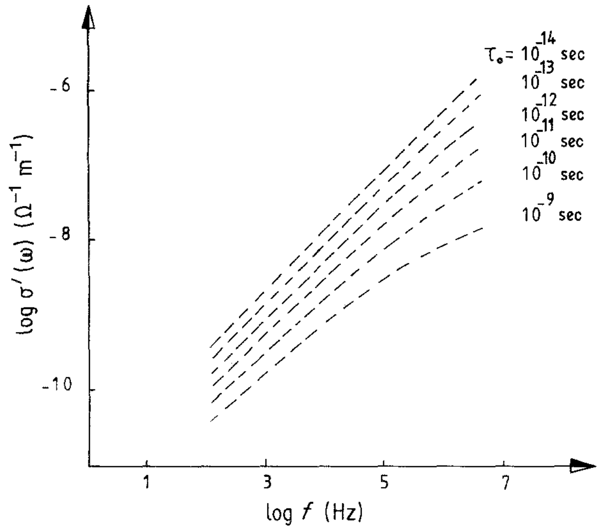

Figure 3 Numerical calculation of the polarization conductivity, for different values of τ_0.

This expression substituted into Equation 9 leads to

$$\sigma'(\omega) = \frac{\pi N^2}{24}\varepsilon_s\omega\left(\frac{4e^2}{\varepsilon_s W_M}\right)^6 \times \int_{\tau_0}^{\tau_\infty}\left[1 - \frac{kT}{W_M}\ln\left(\frac{\tau}{\tau_0}\right)\right]^{-6}\frac{\omega}{1+\omega^2\tau^2}\,d\tau \qquad (11)$$

We then checked that our numerical integration [17] led to the equation

$$\sigma'(\omega) = A(T)\omega^{s(T)} \qquad (12)$$

The variation of parameter s with T, calculated numerically, is described satisfactorily by the law proposed by Long [16] for single-electron hops

$$s = 1 - \frac{6kT}{W_M + kT\ln(\omega\tau_0)} \qquad (13)$$

We have also shown that W_M has a lower limit below which the validity of the model must be carefully verified [17].

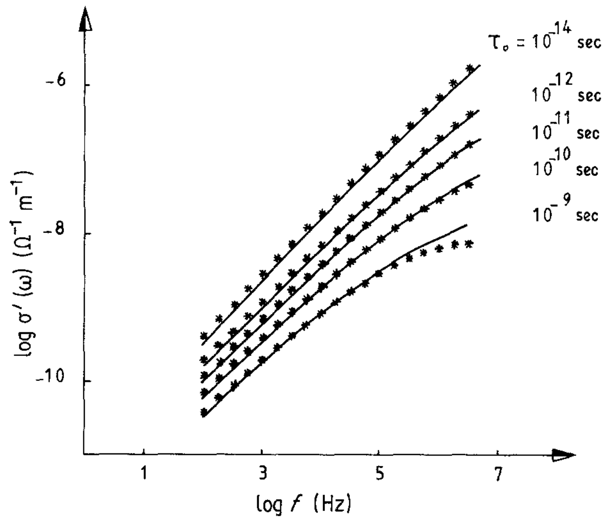

Figure 4 Numerical calculation of the polarization conductivity (solid lines) in comparison to results from the analytical Equation 16 (*).

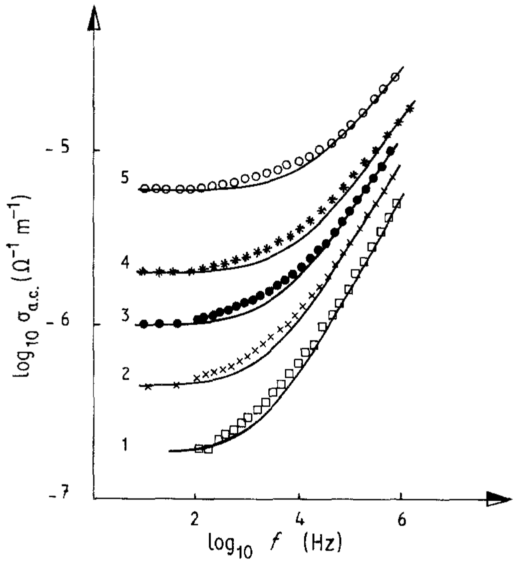

Figure 5 Frequency-dependent conductivity of the carbon (HTT 600° C). (1, T = 165 K; 2, T = 190 K; 3, T = 216 K; 4, T = 233 K; 5, T = 268 K; the solid lines are calculated using the QMT model.)

4.2. Application of the CBH model

This new method of numerical calculation was applied to two series of chalcogenides: the two amorphous molybdenum sulphides treated at 500 and 700° C and the three amorphous tungsten sulphides. In Figs 1 and 2 the experimental measurements are plotted against the theoretical curves obtained by the use of Equations 1 and 11.

It was found that this method also determined the energy value W_M more accurately. The values in Table I are larger than those previously proposed [11], being closer to the d.c. activation energy.

4.3. Use of the QMT model

Pollak and Geballe [9] were the first to propose such a model. Their theory was refined and developed particularly by Mott and Davis [3]. The two following basic hypotheses are the fundamentals of the model.

1. Electron transitions between two sites occur

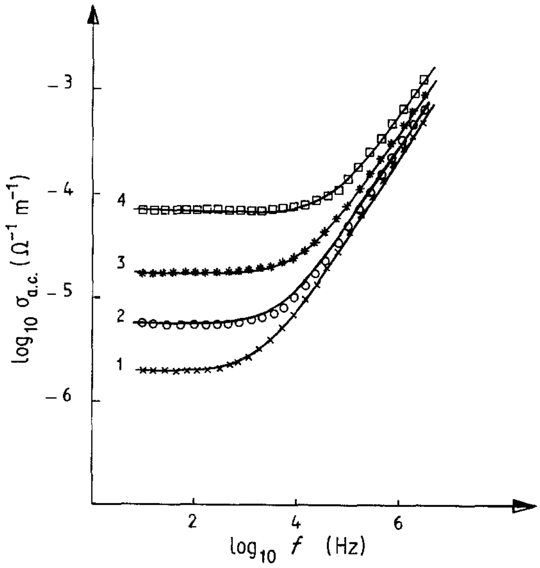

Figure 6 A.c. conductivity of MoS_3 (TT 195° C) as a function of frequency, in comparison to the calculated values (solid lines) using the QMT model. (1, T = 165 K; 2, T = 190 K; 3, T = 216 K; 4, T = 233 K).

TABLE II Values of s and the densities of states $N(E_F)$ for carbon and molybdenum trisulphide (QMT model)

Compound	s	$N(E_F)(\mathrm{eV}^{-1}\,\mathrm{cm}^{-3})$
Carbon (HTT 600° C)	0.61	2.6×10^{19}
MoS_3 (TT 195° C)	0.79	6×10^{20}

by tunnelling through a potential barrier between them. It has been demonstrated that the relaxation time associated with this mechanism takes the form [2, 3, 12]

$$\tau = \tau_0 \exp(2\alpha R) \qquad (14)$$

In this equation, τ_0 has the meaning attributed to it above and α is defined so that $\exp(-\alpha R)$ is the rate at which the wavefunction falls off with distance. R is still the hopping distance.

2. The spatial probability of finding a site at a distance R, from a given site is spherically symmetric (see Equation 8).

It can be shown that the use of these two basic hypotheses leads to [8]

$$\sigma'(\omega) = \frac{\pi N^2 e^2}{6kT}(2\alpha)^{-5}\omega \int_{\tau_0}^{\tau_\infty}\left[\ln\left(\frac{\tau}{\tau_0}\right)\right]^4 \times \frac{\omega}{1+\omega^2\tau^2}\,\mathrm{d}\tau \qquad (15)$$

We have confirmed by our numerical calculation that Equation 15 leads to the functional dependence observed experimentally (Equation 12). To do this, we first considered a fictitious set of samples characterized by $N = 10^{18}\,\mathrm{cm}^{-3}$, $\alpha^{-1} = 0.3\,\mathrm{nm}$; $T = 100\,\mathrm{K}$. We thus assumed that we had measured, as a function of frequency between 1 kHz and 10 MHz, the polarization conductivity of a series of samples characterized by these parameters and by relaxation times τ_0 varying from 10^{-14} to 10^{-9} sec.

The logarithmic representation of the variations of $\sigma'(\omega)$ as a function of frequency is shown in Fig. 3. The behaviour observed experimentally (Equation 12) is reproduced by the calculated curves with the smallest values of τ_0.

As can be seen the slopes of the curves depend on the values of τ_0.

The investigation was continued by comparing the numerical results with those published by Mott and Davis [3] who, with a certain number of approximations, gave an analytical expression for $\sigma'(\omega)$

$$\sigma'(\omega) = A(T)\omega\left[\ln\left(\frac{1}{\omega\tau_0}\right)\right]^4 \qquad (16)$$

This comparison is shown in Fig. 4 where it can be seen that although the behaviour of s as a function of τ_0 is clearly of the same type, agreement is only satisfying for values of τ_0 lower than 10^{-11} sec in the frequency range generally explored.

4.4. Application of the QMT model

We have also used this numerical method to describe the behaviour of a low-temperature anthracene coke (HTT 600° C) (Fig. 5) and an amorphous molybdenum sulphide (MoS_3TT = 195° C) (Fig. 6).

These figures also show the quality of the theoretical fits obtained by numerical calculation of $\sigma'(\omega)$ using Equation 15. The parameters calculated in this way are shown in Table II, where $N(E_F)$ are the densities of states at the Fermi level ($N = kTN(E_F)$).

5. Conclusion

The polarization conductivity was calculated numerically for the models used most commonly to describe hopping conduction.

The compounds studied are characterized by relatively low values of energy, W_M, associated with localized sites. The behaviour of their electronic properties is not accurately described in all cases by the classical approximations. We have, nevertheless, been able to show that the behaviour can be accounted for by the two hopping models when numerical methods are used.

This type of numerical approach could easily be extended to many different compounds, including other chalcogenides, the electrical properties of which display similar behaviour.

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