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ACTIVATION ENERGIES FROM CONDUCTIVITY–TEMPERATURE MEASUREMENTS *

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The experimental determination of activation energies in the electrical conductivity σ as a function of temperature is sometimes difficult, as the Arrhenius plot ($\log\sigma$ versus T^{-1}) may not be linear. This may be due to a process involving several similar activat on energies, to conduction by polarons [1–3], or to variable range hopping of carriers [1,4]. In this paper we discuss a method of analysis of experimental results for $\log\sigma$ versus T^{-1} plots which helps to determine the best transport model [5,6], and which avoids an error which has appeared several times in the recent literature [7–9].

A general expression for dc electrical conductivity in semiconductors and in insulators is

$$\sigma(T) = A(T)\exp\left[-\beta W(T)\right], \tag{1}$$

where T is the temperature, $\beta^{-1} = k_B T$, k_B is the Boltzmann constant, and $A(T)$ and $W(T)$ are assumed to be slowly varying functions of the temperature. For example, several models of conduction [5,6] lead to $A(T) = aT^{-n}$. The usual analysis of the conduction curve by Arrhenius plot calculates the slope, or $W'(T)k_B^{-1}$ where

$$W'(T) = -\partial \ln\sigma/\partial\beta \tag{2}$$

$$= W(T) - \frac{\partial \ln A(T)}{\partial\beta} + \beta\frac{\partial W(T)}{\partial\beta}. \tag{3}$$

If there is reason to believe that A and W are temperature independent, then the slope should be constant, yielding directly the activation energy, W. In the general case, knowledge of $W'(T)$ does not permit the two unknowns A and W to be uniquely determined. Often, however, models of electrical transport place additional constraints on the functions $A(T)$ and $W(T)$, and with these we can

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determine both from a knowledge of $\sigma(T)$. We illustrate this point with two model examples.

(1) *Variable range hopping.* Assuming a general function for the density of electronic states about the Fermi energy

$$N(E) = N_0(E - E_F)^p, \tag{4}$$

where

$$0 < p < \infty,$$

Hamilton [10] has shown that the dc electrical conductivity is related to this density of states by:

$$\sigma(T) = \sigma(0)\exp(-BT^{-[(p+1)/(p+4)]}), \tag{5}$$

Mott's widely quoted $T^{-1/4}$ law corresponds to the case $p = 0$ and to a constant density of states near the Fermi energy [1,4]. An Arrhenius analysis [eq. (3)] yields the function

$$W''(T) = Bk_B\left(\frac{p+1}{p+4}\right)T^{3/(p+4)}. \tag{6}$$

The constants B and p may be independently determined by finding the intercept and the slope, respectively, on a $\log W''$ versus $\log T$ plot. The function $W''(T)$ also gives the hopping energy through the relation [10]

$$\Delta E = 2^{-p/(p+4)}W''. \tag{7}$$

This energy varies continuously from W'' to $W''/2$ as p increases from 0 to a large value. Finally, as a check on the validity of this model, according to Mott [1,4] the energy W'' must satisfy

$$W''(T) < 2^{p/(p+4)}k_BT. \tag{8}$$

(2) *Conduction by small polarons.* Schnakenberg (11) has analysed the non-adiabatic hopping energy W of small polarons at temperatures above $\theta_D/4$, where θ_D is the Debye temperature of the optical phonons of the solid, and he deduced the following high temperature relation:

$$W(T) = W_H\left(\frac{\tanh(\theta_D/4T)}{(\theta_D/4T)}\right) + \frac{W_D}{2}, \tag{9}$$

where W_D and W_H are two constants (disorder energy and high temperature small polaron hopping energy, respectively). Moreover, the conductivity $\sigma(T)$ is given by eq. (1), with the above expression for $W(T)$ and a prefactor, A, which is constant or depends only very weakly on temperature. Fitting the constants of the model using an Arrhenius plot analysis, this involves the energy

$$W''(T) = W'_H\,\mathrm{sech}^2(\theta_D/4T) + W_D/2. \tag{10}$$

We determine the parameters W_H, W_D and θ_D in a two step process. First

we assume that W_D is zero an
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W'' versus $\mathrm{sech}^2(\theta_D/4T)$ pl
determined using eq. (9). R
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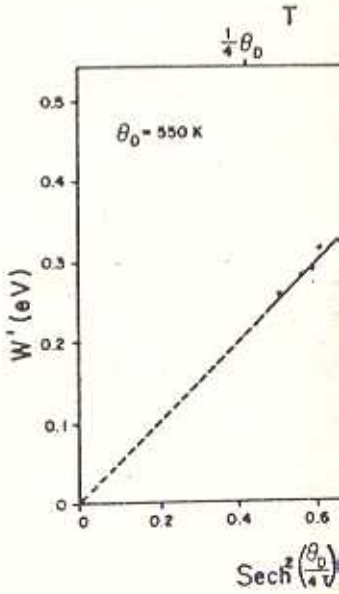

Fig. 1. Best fit to the small polaron
mica as shown by a plot of $W''(T)$
$W_H = 0.5$ eV, $W_D = 0.0$ eV and θ_D

we assume that W'_D is zero and calculate θ_D and W'_H from the slope of a W'' versus $T^{-\frac{1}{2}}$ plot for those temperatures above $\theta_D/4$. Second we find better values for W'_H and W'_D from the slope and the intercept of the straight line in a W'' versus $\mathrm{sech}^2(\theta_D/4T)$ plot. The hopping energy $W(T)$ may then be determined using eq. (9). Recently, several authors [7–9] have made the mistake of calculating θ_D from eq. (9), instead of eq. (10) for $W''(T)$, in the analyses of their Arrhenius plots. This leads to values of the Debye temperature θ_D which are a factor of up to 2 too large.

As an example of the analyses described above, we have applied the two models just described to the conductivity–temperature data for biotite mica [12,13]. Applying the variable range hopping model, we indeed find that $\log\sigma$ is linearly dependent upon T at high temperature, and varies roughly as $T^{1/4}$ at low temperature. However, $W''(T)$ thus obtained does not satisfy the relation [8]. In addition, the resulting values of W'' and of B lead to unreasonable values for the hopping length and of the density of states at the Fermi energy [12]. In contrast, use of the small polaron model to calculate $W''(T)$ yields physically plausible values, $W'_H = 0.5$ eV, $W'_D = (0 \pm 0.05)$ eV and $\theta_D = 550$ K. In fig. 1 we show the fit of $W''(T)$ versus $\mathrm{sech}^2(\theta_D/4T)$, using these values of the parameters. The excellent fit supports both the methodology for the parameters, as well as the model of conduction in biotite mica.

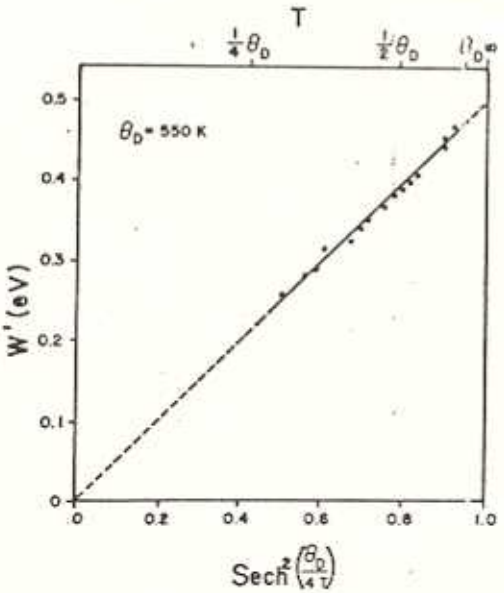

Fig. 1. Best fit of the small polaron hopping model to conductivity–temperature data for biotite mica as shown by a plot of $W''(T)$ versus $\mathrm{sech}^2(\theta_D/4T)$. The values of the parameters are $W'_H = 0.5$ eV, $W'_D = 0.0$ eV and $\theta_D = 550$ K.

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LOW-TEMPERATURE THER
VYCOR

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Measurements [1] of the low and of amorphous polymers ha strongly and explicitly frequen and that this frequency depend istic "plateau" (roughly temp amorphous materials. This con [2,3]. In brief, the strong frequ als serve as low-pass filters fo 30 K, the heat is carried by ph of ≈ 1 K rather than 30 K. thermal conductivity of amor ter, $d < \lambda$. If indeed long-w scattering of phonons by the such holes and thus served as were available only for temper [5] to 100 K, and for two diff paper is to determine if the m

Porous Vycor is produced glass. The remaining phase is from 35 to 75 Å in diamete available thermal conductivit The values of d and r for th shown in fig. 1 are data for s

The plan is to obtain a fr the vitreous silica data, then s to see if the Vycor data can

* The comment in section 4 of ref. measurements, is not correct.

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