A phenomenological model for the Meyer-Neldel rule

Dyre, J. C.

Publication date:
1985

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (APA):
Dyre, J. C. (1985). *A phenomenological model for the Meyer-Neldel rule*. Roskilde Universitet.

TEKST NR 116 1985

A PHENOMENOLOGICAL MODEL FOR THE MEYER-NELDEL RULE

Jeppe C. Dyre

Manuscript submitted to J. Phys. C

TEKSTER fra

IMFUFA ROSKILDE UNIVERSITETSCENTER
INSTITUT FOR STUDIET AF MATEMATIK OG FYSIK SAMT DERES FUNKTIONER I UNDERVISNING, FORSKNING OG ANVENDELSER

IMFUFA, Roskilde Universitetscenter, Postbox 260, 4000 Roskilde

A PHENOMENOLOGICAL MODEL FOR THE MEYER - NELDEL RULE

af Jeppe C. Dyre

IMFUFA tekst nr. 116/85 32 sider ISSN 0106-6242

Abstract

In this paper it is argued that the generality of the Meyer-Neldel rule compels one to adopt a phenomenological approach if a universally valid model is aimed at. It is shown that there exists only one possible phenomenological model. This model is based on an exponential probability distribution of energy barriers. The model predicts a power-law frequency-dependence of the a.c. conductivity with the exponent s given by $s = 1-T/T_o$ where T_o is the characteristic temperature of the Meyer-Neldel rule. It is conjectured that the exponential energy barrier distribution derives from a "glass transistion" at T_o. The generalization of the model to account for the compensation effect is briefly discussed examplified by the case of heterogeneous catalysis.

1. Introduction

Semiconductors are characterized by the temperature-dependence of their electrical conductivity. If $\sigma(0)$ denotes the d.c. conductivity one usually writes

$$\sigma(0) = A \; e^{-\Delta E/kT} \tag{1}$$

where ΔE is the activation energy, k is the Boltzmann constant, T is the temperature, and A is the so-called preexponential factor. Almost 50 years ago, Meyer and Neldel (1937) found for some oxide semiconductors that when the semiconductor is prepared or annealed under different conditions, the activation energy varies and that A depends exponentially on ΔE. Their discovery has become known as the Meyer-Neldel (MN-) rule. It states that the d.c. conductivity is given by

$$\sigma(0) = \sigma_{00} \; e^{\Delta E/kT_0} \; e^{-\Delta E/kT} \tag{2}$$

where σ_{00} and T_0 are constants within a class of related semiconductors.

The MN-rule is an empirical relation which has been observed in very many different semiconductors. These include single-crystal and polycrystalline semiconductors, amorphous semiconductors, organic semiconductors, and even ionically conducting crystals and glasses (Rosenberg, Bhowmik, Harder and Postow 1968, Roberts 1971, Carlson and Wronski 1979, Dosdale and Brook 1983). The rule applies to chemically closely related semiconductors or to a single semiconductor prepared in various

ways. For instance one may vary the degree of non-stoichiometry, the dopant concentration, the oxygen partial pressure at annealing, etc. The MN-rule seems to be an almost universal characteristic of semiconductors which have in common only the property of being inhomogeneous from some point of view (Irsigler, Wagner and Dunstan 1983). But the relation is even more general than that. In a number of rate processes it is found that the preexponential factor A of the reaction rate depends itself exponentially on the activation energy: $A \propto \exp(\Delta E/kT_o)$, just as in eqn. (2). This phenomenon is usually referred to as the compensation effect, but it has also been called the Constable law, the isokinetic relationship or the θ-rule (Exner 1964, Khait 1983). A thoroughly studied example is the compensation effect in heterogeneous catalysis which has been reviewed by Galwey (1977). The compensation effect has also been observed by e.g. thermionic emission of electrons from a metal (Vanselow 1985), diffusion in solids (Shinar, Davidov and Shaltiel 1984), annealing time of irradiated silicon (Fang 1969), viscosity of aqueous solutions (Good and Stone 1972), decomposition of solids (Zsako,Varhelyi, Varhelyi and Liptay 1981), and a number of biophysical, biochemical and biological systems (Rosenberg, Kemeny, Switzer and Hamilton 1971, Tomlinson 1983).

In this paper the starting point is the observation that one is forced to adopt a phenomenological approach if the many occurences of the MN-rule are believed to have a single common origin. The occurence of the compensation effect in other contexts even more emphasizes the need for a phenomenological approach. While the paper is almost exclusively about the MN-rule in semiconductors, the model to be proposed can be generalized immediately to deal with the compensation effect in other

rate processes, as will be briefly commented upon in sec. 6.

The paper is organized as follows. Section 2 argues for the need for a phenomenological model and derives the basic feature of such a model, an exponential probability distribution of energy barriers. In section 3 the simple mathematics of the model is developed. It will be shown that the model predicts a correlation between the MN-rule and the a.c. properties of the semiconductors. In section 4 the model predictions are compared to experiments. In section 5 it is conjectured that the exponential energy barrier distribution is a consequence of a glass transistion. Section 6 deals with the generalization of the model to deal with the compensation effect in other rate processes, examplified by the case of heterogeneous catalysis. A final discussion is given in section 7.

2. The need for a phenomenological approach

Several models have been proposed to explain the MN-rule. Busch (1950) suggested that the MN-rule in extrinsic broad band semiconductors is due to a freezing of the donor concentration during cooling after the preparation. The MN-rule in amorphous or polycrystalline semiconductors may derive from an exponential tailing of the majority band states as suggested by Roberts (1971), or it may be due to a long-ranged electrostatic random potential (Overhof 1984). As regards the MN-rule in organic semiconductors, Kemeny and Rosenberg (1970) proposed a model where electrons or polarons tunnel through intermolecular barriers from activated energy states of the organic molecu-

les. For ionic conductors it has been argued that the MN-rule is an approximate relation valid for ionic crystals with either Frenkel, Schottky or interstitial disorder (Dosdale and Brook 1983). It has even been suggested that the MN-rule may be a spurious effect due to a thin rectifying layer at the electrode-solid interface (Roberts 1971).

It is of course perfectly possible that the MN-rule has many different explanations, each valid for only a limited class of solids. But in view of the generality of the phenomenon it seems more likely that there is a single, general explanation. However, if a single model of the MN-rule is to be universally valid, it can not relate directly to the microscopic details of the conduction process; it must be a phenomenological model. This is an important, though obvious, conclusion. It will be shown below that once the phenomenological approach is accepted there is only one possible model.

Proceeding now to derive the basic feature of a phenomenological model for the MN-rule, we remind that the rule has been observed in both electronically, polaronically and ionically conducting solids. The only way to describe these different cases by a single model is to use a hopping model, i. e. to regard the conduction process as mediated by hopping of localized charge carriers ("quasiparticles"). The single common feature of the many occurences of the MN-rule is an element of disorder from some point of view (Dewsberry 1975, Irsigler et al. 1983). Disorder can easily be built into a hopping model via a probability distribution $p(\tau)$ of waiting times τ at each quasiparticle site (Scher and Lax 1973). It is known from a. c. conductivity measurements that there is always a maximum waiting time τ_{max}, corresponding to the frequency

below which the conductivity becomes frequency-independent. On the other hand, there is no minimum waiting time τ_{min} of any relevance to this problem (i.e. $\tau_{min} \cong 10^{-12}$ s). Thus, in the phenomenological model a solid is completely characterized by the two entities: $p(\tau)$ and τ_{max}. Now, a class of MN-related solids must have something in common. It is physically obvious that the d.c. conductivity depends strongly on τ_{max} so the common entity must be $p(\tau)$.

Having reached the conclusion that different MN-related solids have the same $p(\tau)$ but different τ_{max}, the next step is to ask what can be learned about $p(\tau)$ from eqn. (2) - the Meyer-Neldel rule. The d.c. conductivity is proportional to the diffusion constant which by Einsteins equation is proportional to the mean-square displacement per unit time of a quasiparticle. The d.c. conductivity is thus proportional to $\lim_{N\to\infty} N/\tau_N$ where τ_N is the time taken for N jumps, that is

$$\sigma(0) \propto \langle \tau \rangle^{-1} \tag{3}$$

where $\langle\ \rangle$ denotes an average over $p(\tau)$ (all jump-jump correlations are ignored). The quasiparticle jumps are thermally activated so τ is determined by an energy barrier $\Delta E'$:

$$\tau = \tau_0\, e^{\Delta E'/kT} \tag{4}$$

where τ_0 is a microscopic time ($\tau_0 \cong 10^{-12}$ s) . The maximum waiting time τ_{max} corresponds to a maximum energy barrier ΔE_τ , while the minimum energy barrier is approximately equal to zero because $\tau_{min} \cong \tau_0$. If the distribution of energy barriers corresponding to $p(\tau)$ is denoted by

$p(\Delta E')$ we now find by combining eqns. (2), (3) and (4)

$$e^{-\Delta E/kT_0}\, e^{\Delta E/kT} \propto \int_0^{\Delta E_\tau} e^{\Delta E'/kT}\, p(\Delta E')\, d(\Delta E') \qquad (5)$$

which is valid for each sample, i.e. for varying ΔE. Taking the derivative of this equation with respect to ΔE one obtains

$$e^{-\Delta E/kT_0}\, e^{\Delta E/kT} \propto e^{\Delta E_\tau/kT}\, p(\Delta E_\tau)\, \frac{d\Delta E_\tau}{d\Delta E} \qquad (6)$$

The constant of proportionality depends weakly on T and ΔE_τ but this is unimportant compared to the exponentials and it will be ignored. By considering the temperature-dependence of both sides of eqn. (6), one finds that $\Delta E = \Delta E_\tau$. This is a manifestation of the above mentioned fact that $\sigma(0)$ and τ_{max} are strongly correlated. Equation (6) now becomes

$$p(\Delta E') \propto e^{-\Delta E'/kT_0} . \qquad (7)$$

Thus, once the phenomenological approach is accepted one is led to a unique model for the MN-rule based on an exponential distribution of energy barriers. It is not surprising that the mathematics involved is very similar to the derivation of the MN-rule from the assumption of exponential band tails (Roberts 1971, Cohen, Economou and Soukoulis 1984), here we have essentially just reversed their argumentation.

3. The model

It is easy to see that variations in quasiparticle jump distance are of little importance compared to the large variations in waiting times. This fact may be built into the model by adopting the Scher-Lax approach (1973) and regard the disordered semiconductor as a regular lattice with randomly varying jump frequencies, and this approach is adopted here. It is convenient to speak of jump frequencies γ instead of waiting times, these two quantities are related by $\gamma = \tau^{-1}$ so the jump frequency is given by

$$\gamma = \gamma_0 \, e^{-\Delta E'/kT} \tag{8}$$

where γ_0 is the attempt frequency ($\cong 10^{12}$ s^{-1}) and $\Delta E'$ is the energy barrier.

As mentioned, the MN-rule is observed in disordered semiconductors. This is the same class of solids that is known to show strong frequency dispersion of the conductivity, and therefore it is of interest to evaluate the entire frequency-dependent conductivity of the model, $\sigma(\omega)$. This quantity can be calculated by the CTRW approximation, the simplest possible non-trivial mean-field approximation. In the CTRW $\sigma(\omega)$ is given by (Scher and Lax 1973, Odagaki and Lax 1981)

$$\sigma(\omega) = \frac{C}{T}\left[-i\omega + \left\langle \frac{1}{\gamma + i\omega} \right\rangle^{-1}\right] \tag{9}$$

where $\langle\ \rangle$ denotes an average over the jump frequency probability distribution $p(\gamma)$, and C is a constant depending on the quasiparticle concentration, average jump distance, etc.

The jump frequency distribution is really a probability density: $p(\gamma) \equiv d\tilde{p}/d\gamma$. From this we find by means of eqns. (7) and (8)

$$p(\gamma) = \frac{d\tilde{p}}{d\gamma} = \frac{d\tilde{p}}{d\Delta E'} \frac{1}{\frac{d\gamma}{d\Delta E'}} \propto e^{-\Delta E'/kT_0} \frac{1}{\gamma} \propto \gamma^{-s} \qquad (10)$$

where

$$s = 1 - T/T_0 \ . \qquad (11)$$

The maximum jump frequency is γ_0 (corresponding to $\Delta E'_{min} = 0$) while the minimum jump frequency is given by

$$\gamma_{min} = \gamma_0 e^{-\Delta E/kT} \qquad (12)$$

where ΔE as in sec. 2 is the maximum energy barrier. The normalized jump frequency distribution is given by

$$p(\gamma) = \frac{1-s}{\gamma_0} \left(\frac{\gamma}{\gamma_0} \right)^{-s} . \qquad (13)$$

Here it has been assumed that $\gamma_{min} << \gamma_0$ which is valid in all cases of interest and will be assumed throughout the paper.

Proceeding now to calculate the conductivity we find for the d.c. conductivity

$$\sigma(0) = \frac{C}{T} \langle \gamma^{-1} \rangle^{-1} = \frac{C}{T} \frac{s}{1-s} \gamma_0 \left(\frac{\gamma_{min}}{\gamma_0} \right)^s \qquad (14)$$

or

$$\sigma(0) = \frac{C}{T} \frac{s}{1-s} \gamma_0 e^{\Delta E/kT_0} e^{-\Delta E/kT} \ . \qquad (15)$$

As expected we recover the MN-rule. There is a factor of T^2 in the denominator differing from eqn. (2), but this is almost unobservable compared to the strong temperature-dependence of the Boltzmann factor. The a.c. conductivity is independent of frequency for $\omega << \gamma_{min}$ and equal to $\sigma(0)$. For frequencies around γ_{min} the conductivity begins to increase. In the limit $\omega >> \gamma_{min}$ (but still $\omega << \gamma_0$) it is easy to calculate $\sigma(\omega)$. In this regime one finds

$$\left\langle \frac{1}{\gamma + i\omega} \right\rangle \simeq \frac{1-s}{\gamma_0} \int_0^\infty \frac{(\gamma/\gamma_0)^{-s}}{\gamma + i\omega} d\gamma = \frac{1}{\gamma_0} \frac{(1-s)\pi}{\sin(s\pi)} \left(\frac{i\omega}{\gamma_0}\right)^{-s} \qquad (16)$$

and since the $i\omega$-term of eqn. (9) is negligible, $\sigma(\omega)$ is simply given by

$$\sigma(\omega) = \frac{C}{T} \gamma_0 \frac{\sin(s\pi)}{(1-s)\pi} \left(\frac{i\omega}{\gamma_0}\right)^s, \quad \gamma_{min} << \omega << \gamma_0 . \qquad (17)$$

Thus a power-law frequency-dependence of the conductivity results, with the exponent $s = 1 - T/T_0$. It must be emphasized, however, that $\sigma(\omega) \propto \omega^s$ with $s = 1 - T/T_0$ is a direct consequence of eqn. (13); the CTRW approximation enters only in the calculation of the constant of proportionality.

4. The phenomenological model and the experimental situation

As shown above, the phenomenological model implies a power-law frequency-dependence of the a.c. conductivity. This is a striking prediction which can be easily checked experimentally, it seems. And indeed, all disordered semiconductors exhibits an ω^s-behaviour of the a.c. conductivity where s is always

less than one and always goes to one as T goes to zero (Jonscher 1977, Long 1982). Still, these experimental findings can not be taken as evidence for the model. The reason is the following. For most solids $\Delta E/T_o$ is not very much larger than one and therefore it is necessary to go to temperatures much below T_o in order to observe a power-law behaviour of $\sigma(\omega)$ covering a wide frequency range. But at low temperatures, the above model is hard to distinguish from another phenomenological model which has nothing to do with the MN-rule. This model, which formally corresponds to the $T_o \to \infty$ limit of the above model, predicts that (Dyre 1985a)

$$\sigma(\omega) = \sigma(0)\,\frac{i\omega\tau}{\ln(1+i\omega\tau)}\,. \qquad (18)$$

This formula implies an a.c. conductivity which is very close to a power-law ω^s where s at low temperatures is given by (Dyre 1985b)

$$s = 1 - T/\tfrac{1}{2}\Delta E\,. \qquad (19)$$

Here ΔE as usual denotes the activation energy of $\sigma(0)$. Obviously, accurate measurements of the a.c. conductivity are necessary in order to distinguish the MN-phenomenological model from the model behind eqn. (18). To make things even worse, it seems that no measurements at all of $\sigma(\omega)$ has been carried out on the same samples that has been reported to obey the MN-rule.

The superionic conductor Na β-alumina is a promising candidate for the verification of the phenomenological model. Although the MN-rule has not been observed in Na β-alumina, we

expect the MN-rule to apply at low temperatures with T_o around 250 K. This prediction is based on the a.c. conductivity measurements of Almond and West (1981). Their data has been carefully analysed by Macdonald and Cook (1984) and they find values of s between 0,35 and 0,72 which turn out to obey eqn. (11) with $T_o \cong 250$ K . A search for the MN-rule in the low-temperature d.c. conductivity of Na β-alumina samples would be very interesting.

5. The Meyer-Neldel rule as a consequence of a glass transistion

In this section the origin of the MN-rule is discussed. First one may ask whether T_o is to be interpreted as a real physical temperature or whether kT_o is just a characteristic energy. The latter point of view is held by the workers postulating exponential band tails (Roberts 1971, Adler 1982, Cohen et al. 1984) and by Kemeny and Rosenberg (1970) who link T_o to the Debye temperature which really is an energy scale. Here, we shall suggest that T_o <u>is</u> a real physical temperature, namely a glass transistion temperature.

Remember that the MN-rule implies that the d.c. conductivity at $T = T_o$ is independent of ΔE . According to the phenomenological model, as T rises towards T_o the deepest energy minima become less important for the determination of $\sigma(0)$ and right at $T = T_o$ they are not important at all. This is reflected by the fact that $p(\gamma) \propto \gamma^{-s}$ becomes $p(\gamma) = \text{const.}$ at $T = T_o$. When the deepest energy minima loose their importance it is obvious that $\sigma(0)$ becomes independent of ΔE, the maximum

energy barrier. In the $\Delta E' \to 0$ limit, energy maxima and energy minima are indistinguishable so the population of energy maxima becomes non-vanishing at $T = T_o$. This means that the picture of activated conductivity breaks down in the setting of an exponential energy barrier distribution, so that the model does not apply for $T > T_o$.

What happens at T_o is hinted at by the exponential energy barrier distribution itself. Since on the average $\Delta E' = \text{const.} - E'$, where E' is the energy of the state which has the barrier $\Delta E'$ to its surrounding states, we find immediately from eqn. (7)

$$n(E') \propto e^{E'/kT_o} \tag{20}$$

where $n(E')$ is the density of energy levels. It must be emphasized that eqn. (20) refer to the quasiparticle-lattice interaction energy and does not include any quasiparticle "kinetic energy". A macroscopic system with the density of energy levels given by eqn. (20) undergoes a phase transistion at $T = T_o$ to a state of zero entropy (a Gibbs-DiMarzio glass transistion (1958)). The system is "frozen". A quasiparticle is only a microscopic system, but still eqn. (20) implies that the quasiparticle energy fluctuations decrease drastically below T_o. It is an obvious guess that what happens at T_o is that the relevant lattice degrees of freedom freeze, so that the quasiparticles for $T<T_o$ are unable to exchange potential energy with the lattice. By freezing is not meant the crystallization of the liquid state, of course, but the freezing-in of the various kinds of lattice defects that determine the quasiparticle energy. When the lattice freezes, the quasiparticle-lattice interaction energy E' becomes a function of the quasiparticle coordinates only. This function is more or less random in space and eqn. (20) then just expresses the pro-

bability of finding energy E' at a given quasiparticle position. In summary, it is conjectured that the MN-rule and eqn. (20) are consequences of a frustration of thermal equilibrium at T_o . The frustration takes place on cooling at the sample preparation. If this picture is correct, the element of disorder common to all occurences of the MN-rule simply derives from a freezing of thermal disorder at T_o .

A frustration of thermal equilibrium can be referred to as a glass transistion. The concept is here used in a generalized sense, often one only speaks of a glass transistion in connection with the solidification of supercooled liquids. The idea that the MN-rule is due to a glass transistion, is not new. Busch (1950) suggested that the MN-rule for extrinsic semiconductors derives from a freezing of the donor concentration during cooling after the sample preparation (Metselaar and Oversluizen 1984). This idea has been generalized here to the conjecture that the MN-rule universally is a consequence of a glass transistion.

6. Generalization of the model. A model for the compensation effect in heterogeneous catalysis.

The topic of this section is the generalization of the phenomenological model to deal with the compensation effect in other contexts than electrical conductivity. By the compensation effect is meant the phenomenon that the reaction rate K for a class of related rate processes is given by

$$K = \text{const.}\, e^{\Delta E/kT_o}\, e^{-\Delta E/kT} \quad . \tag{21}$$

In this more general setting T_o is often referred to as the isokinetic temperature. To be specific we shall discuss only the compensation effect in heterogeneous catalysis (Cremer 1955, Sinfelt 1969, Galwey 1977), but it is straightforward to

generalize the below considerations to deal with other cases.

In the present model heterogeneous catalysis is regarded as the result of many possible reaction sequences, each sequence consisting of many intermediate steps. The intermediate states are situated at local energy minima in the abstract reaction coordinate space and an intermediate reaction is a thermally activated "jump" between two adjacent minima. This is analogous to quasiparticle jumps in ordinary space and the overall reaction rate K becomes the analogue of $\sigma(0)$. Because of the complexity in the model, a statistical approach is needed for the calculation of K. Analogously to the MN-rule case it can now be shown that an exponential energy barrier distribution implies eqn. (21). As in sec.5, the exponential distribution is conjectured to derive from a glass transistion at T_o. The glass transistion is here the freezing of the relevant catalyst surface degrees of freedom - they determine the energy function in reaction coordinate space.

If this model is correct there is no such thing as <u>the</u> mechanism of a heterogeneous catalytic reaction. Many different reaction sequences contributes to the overall reaction, and the whole thing is so complex that a statistical approach is necessary. Actually, the complexity of heterogeneous catalysis is commonly recognized to the extent that the mechanism of catalysis is often referred to as "black magic". Once the statistical approach is accepted, however, the argumentation of sec. 2 applies from which it can be concluded that the model is unique in the sense that only an exponential energy barrier distribution is possible if the compensation effect is to be reproduced (assuming $\Delta E'_{min} = 0$).

The model implies that interesting time-dependent phenomena

must be present in connection with the compensation effect. As a consequence of the exponential barrier distribution, it is predicted that power-law time- or frequency-dependence should be observed in chemical relaxation experiments with an exponent s given by eqn. (11). Further discussion of this point will appear elsewhere.

7. Summary and discussion

The MN-rule is a quite universal phenomenon and this fact emphasizes the need for a phenomenological model. As shown in sec. 2, once the phenomenological approach is accepted there is only one possible model, namely that based on an exponential distribution of energy barriers. The exponential barrier distribution is well-known. It has been used e.g. for describing a.c. conductivity of hollandite (Bernasconi, Beyeler, Strässler and Alexander 1979), dispersive transport in a-Si:H (Hvam and Brodsky 1981), structural relaxation of amorphous germanium (Olsen), dielectric polarisation phenomena in glasses (Thurzo, Barančok, Doupovec, Mariani and Jančí 1975), and, in the form of exponential band tails, to explain the MN-rule (Roberts 1971, Cohen et al. 1984). A thorough study of the exponential energy barrier distribution was given by Macdonald (1963). The phenomenological model thus contains few new ideas, it is just an attempt to present a coherent picture of conductivity in MN-semiconductors. Though the model was constructed to explain the d.c. properties, it implies a perhaps surprising prediction of a correlation between the MN-rule and the a.c.

properties: $\sigma(\omega) \propto \omega^s$ where $s = 1-T/T_o$ (sec. 3).

The experimental situation is complex and there exists no conclusive evidence in favour of the model. The MN-rule is observed in disordered semiconductors, exactly the same class of solids that is known to show a power-law frequency-dependence of the a.c. conductivity. This, and the fact that the exponent s always obeys $s<1$ and $s \to 1$ for $T \to 0$, is in agreement with model predictions, but it can not be taken as evidence for the model as discussed in sec. 4. Careful experiments are needed, for instance measuring $s(T)$ as $T \to 0$. In one case, for the important semiconductor a-Si:H, observed values of s close to one at $T \cong 300$ K (Shimakawa, Watanabe, Yano and Kondo 1983) do not agree with the model because the various reported values of T_o for this solid are all below 1000 K (Fritzsche 1980).

In sec. 5 it was suggested that the MN-rule is a consequence of a glass transistion. It was conjectured that the exponential barrier distribution follows from a freezing-in of the lattice degrees of freedom defing the quasiparticle energy, i.e. of the various relevant lattice defects. In this picture both the MN-rule and the conductivity dispersion are ultimately consequences of broken ergodicity (Palmer 1982).

At $T = T_o$ the phenomenological model breaks down and a kind of phase transistion is expected. In particular, the conductivity becomes frequency-independent at this temperature. Usually, it is not possible to measure at this high temperature. Some experiments at T_o have been carried out, though, and there are signs of something happening at T_o as signalled by a discontinuous change of activation energy (fig. 1 of Weichman and Kužel (1970), fig. 1 of Irsigler et al. (1983)). Further experiments near T_o would be very interesting.

The MN-rule is only one manifestation of the very general compensation effect. The need for a universal explanation is increasingly realized, and this problem has been addressed by several authors recently suggesting various modifications of rate theory (Conner 1982, Peacock-Lőpez and Suhl 1982, Khait 1983, McCoy 1984). In this paper rate theory has been assumed to apply. It is straightforward to generalize the phenomenological model to deal with the compensation effect in general, as was discussed in sec. 6 examplified by the case of heterogeneous catalysis. Quasiparticle jumps in ordinary space are replaced by reactions in the abstract reaction coordinate space, but the exponential energy barrier distribution remains unchanged. The basic assumptions of the generalized model are: 1) the existence of an element of disorder, and 2) that the overall reaction is the result of many reaction sequences acting in parallel, each sequence involving many intermediate steps. If these assumptions are accepted, the overall reaction rate becomes the analogue of the d.c. conductivity of the MN-rule, and the uniqueness of the generalized model can be proved just as in sec. 2.

As in sec. 5 it may be argued that a glass transistion at T_o is the origin of the exponential energy barrier distribution of the generalized model. It is interesting that the compensation effect almost always involves solids. These solids must contain an element of disorder deriving from a freezing of thermal disorder at T_o, if the ideas of sec. 5 are correct. As regards the observation of the compensation effect in liquid solutions (Leffler 1955), it is hard to see how the glass transistion ideas can apply, though.

The generalized model predicts a power-law time-dependence of chemical relaxation experiments and also that a kind of

phase transistion must occur at T_o . Further discussion of the phenomenological model in this more general setting is the subject of a future publication.

Acknowledgement

Inspiration from N B Olsen's unpublished model of structural relaxation of amorphous germanium, both as regards the exponential barrier distribution and the glass transistion idea of its origin, is gratefully acknowledged.

References

Adler D, 1982, Solar Energy Mater. 8, 53.

Almond D P and West A R, 1981, Solid State Ionics 3/4, 73.

Bernasconi J, Beyeler H U, Strässler S and Alexander S, 1979, Phys. Rev. Lett. 42, 819.

Busch G, 1950, Z. Angew. Math. Phys. 1, 81.

Carlson D E and Wronski C R, 1979, Amorphous Semiconductors, Topics in Applied Physics, Vol. 36, ed. M H Brodsky (Springer, New York, 1979), p. 287.

Cohen M H, Economou E N and Soukoulis C M, 1984, J. Non-Cryst. Solids 66, 285.

Conner W C, 1982, J. Catal. 78, 238.

Cremer E, 1955, Adv. Catal. 7, 75.

Dewsberry R, 1975, J. Phys. D 8, 1797.

Dosdale T and Brook R J, 1983, Solid State Ionics 8, 297.

Dyre J C, 1985a, Phys. Lett. 108A, 457.

Dyre J C, 1985b, Proceedings of the Third International Conference on the Structure of Non-Crystalline Materials, J. Physique Colloq., to appear.

Exner O, 1964, Nature 201, 488.

Fang P H, 1969, Phys. Lett. 30A, 217.

Fritzsche H, 1980, Solar Energy Mater. 3, 447

Galwey A K, 1977, Adv. Catal. 26, 247.

Gibbs J H and DiMarzio E A, 1958, J. Chem. Phys. 28, 373.

Good W and Stone J, 1972, Electrochim. Acta 17, 1813.

Hvam J M and Brodsky M H, 1981, Phys. Rev. Lett. 46, 371.

Irsigler P, Wagner D and Dunstan D J, 1983, J. Phys. C 16, 6605.

Jonscher A K, 1977, Nature 267, 673.

Kemeny G and Rosenberg B, 1970, J. Chem. Phys. 53, 3549.

Khait Y L, 1983, Phys. Rep. 99, 237.

Leffler J E,1955, J. Org. Chem. 20, 1202.

Long A R, 1982, Adv. Phys. 31, 553.

Macdonald J R, 1963, J. Appl. Phys. 34, 538.

Macdonald J R and Cook G B, 1984, J. Electroanal. Chem. 168, 335.

McCoy B J, 1984, J. Chem. Phys. 80, 3629.

Metselaar R and Oversluizen G, 1984, J. Solid State Chem. 55, 320.

Meyer W and Neldel H, 1937, Z. Techn. Phys. 12, 588.

Odagaki T and Lax M, 1981, Phys. Rev. B 24, 5284.

Olsen N B, unpublished.

Overhof H, 1984, J. Non-Cryst. Solids 66, 261.

Palmer R G, 1982, Adv. Phys. 31, 669.

Peacock-Lőpez E and Suhl H, 1982, Phys. Rev. B 26, 3774.

Roberts G G, 1971, J. Phys. C 4, 3167.

Rosenberg B, Bhowmik B B, Harder H C and Postow E, 1968, J. Chem. Phys. 49, 4108.

Rosenberg B, Kemeny G, Switzer R C and Hamilton T C, 1971, Nature 232, 471.

Scher H and Lax M, 1973, Phys. Rev. B 7, 4491.

Shimakawa K, Watanabe A, Yano Y and Kondo A, 1983, J. Non-Cryst. Solids 59-60, 1023.

Shinar J, Davidov D and Shaltiel D, 1984, Phys. Rev. B 30, 6331.

Sinfelt J H, 1969, Catal. Rev. 3, 175.

Thurzo I, Barančok D, Doupovec J, Mariani E and Jančí J, 1975, J. Non-Cryst. Solids 18, 129.

Tomlinson E, 1983, Int. J. Pharm. 13, 115.

Vanselow R, 1985, Surface Sci. 149, 381.

Weichman F L and Kužel R, 1970, Can. J. Phys. 48, 63.

Zsako J, Varhelyi M, Varhelyi C and Liptay G, 1981, Thermochim. Acta 51, 277.

1/78 "TANKER OM EN PRAKSIS" - et matematikprojekt.
Projektrapport af Anne Jensen, Lena Lindenskov, Marianne Kesselhahn og Nicolai Lomholt.
Vejleder: Anders Madsen.

2/78 "OPTIMERING" - Menneskets forøgede beherskelsesmuligheder af natur og samfund.
Projektrapport af Tom J. Andersen, Tommy R. Andersen, Gert Kreinøe og Peter H. Lassen.
Vejleder: Bernhelm Booss.

3/78 "OPGAVESAMLING", breddekursus i fysik. Nr. 3 er a jour ført i marts 1984
Lasse Rasmussen, Aage Bonde Kræmmer, Jens Højgaard Jensen.

4/78 "TRE ESSAYS" - om matematikundervisning, matematiklæreruddannelsen og videnskabsrindalismen. Nr. 4 er p.t. udgået.
Mogens Niss.

5/78 "BIBLIOGRAFISK VEJLEDNING til studiet af DEN MODERNE FYSIKS HISTORIE". Nr. 5 er p.t. udgået.
Helge Kragh.

6/78 "NOGLE ARTIKLER OG DEBATINDLÆG OM - læreruddannelse og undervisning i fysik, og - de naturvidenskabelige fags situation efter studenteroprøret".
Karin Beyer, Jens Højgaard Jensen og Bent C. Jørgensen.

7/78 "MATEMATIKKENS FORHOLD TIL SAMFUNDSØKONOMIEN". Nr. 7 er udgået.
B.V. Gnedenko.

8/78 "DYNAMIK OG DIAGRAMMER". Introduktion til energy-bond-graph formalismen.
Peder Voetmann Christiansen.

9/78 "OM PRAKSIS' INDFLYDELSE PA MATEMATIKKENS UDVIKLING". - Motiver til Kepler's:"Nova Stereometria Doliorum Vinarioum".
Projektrapport af Lasse Rasmussen.
Vejleder: Anders Madsen.

10/79 "TERMODYNAMIK I GYMNASIET".
Projektrapport af Jan Christensen og Jeanne Mortensen.
Vejledere: Karin Beyer og Peder Voetmann Christiansen.

11/79 "STATISTISKE MATERIALER"
red. Jørgen Larsen

12/79 "LINEÆRE DIFFERENTIALLIGNINGER OG DIFFERENTIALLIGNINGSSYSTEMER". Nr. 12 er udgået
Mogens Brun Heefelt

13/79 "CAVENDISH'S FORSØG I GYMNASIET".
Projektrapport af Gert Kreinøe.
Vejleder: Albert Chr. Paulsen

14/79 "BOOKS ABOUT MATHEMATICS: History, Philosophy, Education, Models, System Theory, and Works of Reference etc. A Bibliography".
Else Høyrup.

Nr. 14 er p.t. udgået.

15/79 "STRUKTUREL STABILITET OG KATASTROFER i systemer i og udenfor termodynamisk ligevægt".
Specialeopgave af Leif S. Striegler.
Vejleder: Peder Voetmann Christiansen.

16/79 "STATISTIK I KRÆFTFORSKNINGEN".
Projektrapport af Michael Olsen og Jørn Jensen.
Vejleder: Jørgen Larsen.

17/79 "AT SPØRGE OG AT SVARE i fysikundervisningen".
Albert Christian Paulsen.

18/79 "MATHEMATICS AND THE REAL WORLD", Proceedings of an International Workshop, Roskilde University Centre, Denmark, 1978. Preprint.
Bernhelm Booss & Mogens Niss (eds.).

19/79 "GEOMETRI, SKOLE OG VIRKELIGHED".
Projektrapport af Tom J. Andersen, Tommy R. Andersen og Per H.H. Larsen.
Vejleder: Mogens Niss.

20/79 "STATISTISKE MODELLER TIL BESTEMMELSE AF SIKRE DOSER FOR CARCINOGENE STOFFER".
Projektrapport af Michael Olsen og Jørn Jensen.
Vejleder: Jørgen Larsen.

21/79 "KONTROL I GYMNASIET - FORMÅL OG KONSEKVENSER".
Projektrapport af Crilles Bacher, Per S. Jensen, Preben Jensen og Torben Nysteen.

22/79 "SEMIOTIK OG SYSTEMEGENSKABER (1)".
1-port lineært response og støj i fysikken.
Peder Voetmann Christiansen.

23/79 "ON THE HISTORY OF EARLY WAVE MECHANICS - with special emphasis on the role of realitivity".

24/80 a+b "MATEMATIKOPFATTELSER HOS 2.G'ERE".
1. En analyse. 2. Interviewmateriale.
Projektrapport af Jan Christensen og Knud Lindhardt Rasmussen.
Vejleder: Mogens Niss.

Nr. 24 a+b er p.t. udgået.

25/80 "EKSAMENSOPGAVER", Dybdemodulet/fysik 1974-79.

26/80 "OM MATEMATISKE MODELLER".
En projektrapport og to artikler.
Jens Højgaard Jensen m.fl.

27/80 "METHODOLOGY AND PHILOSOPHY OF SCIENCE IN PAUL DIRAC's PHYSICS".
Helge Kragh.

28/80 "DIELEKTRISK RELAXATION - et forslag til en ny model bygget på væskernes viscoelastiske egenskaber".
Projektrapport, speciale i fysik, af Gert Kreinøe.
Vejleder: Niels Boye Olsen.

55/82 "MATEMATISKE MODELLER" - Litteratur på Roskilde Universitetsbibliotek.

En bibliografi.

Else Høyrup.

Vedr. tekst nr. 55/82:
Se også tekst 62/83.

56/82 "ÉN - TO - MANGE" -
En undersøgelse af matematisk økologi.

Projektrapport af Troels Lange.

Vejleder: Anders Madsen.

57/83 "ASPECT EKSPERIMENTET" -
Skjulte variable i kvantemekanikken?

Projektrapport af Tom Juul Andersen.

Vejleder: Peder Voetmann Christiansen.

Nr. 57 er udgået.

58/83 "MATEMATISKE VANDRINGER" - Modelbetragtninger over spredning af dyr mellem småbiotoper i agerlandet.

Projektrapport af Per Hammershøj Jensen & Lene Vagn Rasmussen.

Vejleder: Jørgen Larsen.

59/83 "THE METHODOLOGY OF ENERGY PLANNING".

ENERGY SERIES NO. 7.

Bent Sørensen.

60/83 "MATEMATISK MODEKSPERTISE" - et eksempel.

Projektrapport af Erik O. Gade, Jørgen Karrebæk og Preben Nørregaard.

Vejleder: Anders Madsen.

61/83 "FYSIKS IDEOLOGISKE FUNKTION", som et eksempel på en naturvidenskab - historisk set.

Projektrapport af Annette Post Nielsen.

Vejledere: Jens Høyrup, Jens Højgaard Jensen og Jørgen Vogelius.

62/83 "MATEMATISKE MODELLER" - Litteratur på Roskilde Universitetsbibliotek.

En bibliografi. 2. rev. udgave

Else Høyrup

63/83 "CREATING ENERGY FUTURES: A SHORT GUIDE TO ENERGY PLANNING".

ENERGY SERIES No. 8

David Crossley & Bent Sørensen

64/83 "VON MATHEMATIK UND KRIEG".

Bernhelm Booss og Jens Høyrup

65/83 "ANVENDT MATEMATIK - TEORI ELLER PRAKSIS".

Projektrapport af Per Hedegård Andersen, Kirsten Habekost, Carsten Holst-Jensen, Annelise von Moos, Else Marie Pedersen, Erling Møller Pedersen.

Vejledere: Bernhelm Booss & Klaus Grünbaum

66/83 "MATEMATISKE MODELLER FOR PERIODISK SELEKTION I ESCHERICHIA COLI".

Projektrapport af Hanne Lisbet Andersen, Ole Richard Jensen og Klavs Frisdahl.

Vejledere: Jørgen Larsen og Anders Hede Madsen

67/83 "ELIPSOIDE METODEN - EN NY METODE TIL LINEÆR PROGRAMMERING?"

Projektrapport af Lone Biilmann og Lars Boye

Vejleder: Mogens Brun Heefelt

68/83 "STOKASTISKE MODELLER I POPULATIONSGENETIK" - til kritikken af teoriladede modeller.

Projektrapport af Lise Odgård Gade, Susanne Hansen, Michael Hviid, Frank Mølgård Olsen.

Vejleder: Jørgen Larsen.

69/83 "ELEVFORUDSÆTNINGER I FYSIK" - en test i 1.g med kommentarer

Albert Chr. Paulsen

70/83 "INDLÆRINGS- OG FORMIDLINGSPROBLEMER I MATEMATIK PA VOKSENUNDERVISNINGSNIVEAU"

Projektrapport af Hanne Lisbet Andersen, Torben J. Andreasen, Svend Age Houmann, Helle Glerup Jensen, Keld Fl. Nielsen, Lene Vagn Rasmussen.

Vejleder: Klaus Grünbaum & Anders H. Madsen

71/83 "PIGER OG FYSIK" - et problem og en udfordring for skolen?

Karin Beyer, Sussanne Blegaa, Birthe Olsen, Jette Reich & Mette Vedelsby

72/83 "VERDEN IFØLGE PEIRCE" - to metafysiske essays, om og af C.S. Peirce.

Peder Voetmann Christiansen

73/83 "EN ENERGIANALYSE AF LANDBRUG" - økologisk contra traditionelt

ENERGY SERIES No. 9

Specialeopgave i fysik af Bent Hove Jensen

Vejleder: Bent Sørensen

74/84 "MINIATURISERING AF MIKROELEKTRONIK" - om videnskabeliggjort teknologi og nytten af at lære fysik

Projektrapport af Bodil Harder og Linda Szkotak Jensen.

Vejledere: Jens Højgaard Jensen og Bent C. Jørgensen

75/84 "MATEMATIKUNDERVISNINGEN I FREMTIDENS GYMNASIUM" - Case: Lineær programmering

Projektrapport af Morten Blomhøj, Klavs Frisdahl, Frank Mølgaard Olsen

Vejledere: Mogens Brun Heefelt & Jens Bjørneboe

76/84 "KERNEKRAFT I DANMARK?" - Et høringssvar indkaldt af miljøministeriet, med kritik af miljøstyrelsens rapporter af 15. marts 1984.

ENERGY SERIES No. 10

Af Niels Boye Olsen og Bent Sørensen

77/84 "POLITISKE INDEKS - FUP ELLER FAKTA?" Opinionsundersøgelser belyst ved statistiske modeller

Projektrapport af Svend Age Houmann, Keld Nielsen, Susanne Stender

Vejledere: Jørgen Larsen & Jens Bjørneboe

78/84 "JÆVNSTRØMSLEDNINGSEVNE OG GITTERSTRUKTUR I AMORFT GERMANIUM"

Specialerapport af Hans Hedal, Frank C. Ludvigsen og Finn C. Physant

Vejleder: Niels Boye Olsen

79/84 "MATEMATIK OG ALMENDANNELSE"

Projektrapport af Henrik Coster, Mikael Wennerberg Johansen, Povl Kattler, Birgitte Lydholm og Morten Overgaard Nielsen.

Vejleder: Bernhelm Booss

80/84 "KURSUSMATERIALE TIL MATEMATIK B"

Mogens Brun Heefelt

81/84 "FREKVENSAFHÆNGIG LEDNINGSEVNE I AMORFT GERMANIUM"

Specialerapport af Jørgen Wind Petersen og Jan Christensen

Vejleder: Niels Boye Olsen

82/84 "MATEMATIK- OG FYSIKUNDERVISNINGEN I DET AUTOMATISEREDE SAMFUND"

Rapport fra et seminar afholdt i Hvidovre 25-27 april 1983

Red.: Jens Højgaard Jensen, Bent C. Jørgensen og Mogens Niss

83/84 "ON THE QUANTIFICATION OF SECURITY" nr. 83 er p.t. udgået

PEACE RESEARCH SERIES NO. 1

af Bent Sørensen

84/84 " NOGLE ARTIKLER OM MATEMATIK, FYSIK OG ALMENDANNELSE".

Jens Højgaard Jensen, Mogens Niss m. fl.

85/84 "CENTRIFUGALREGULATORER OG MATEMATIK"

Specialerapport af Per Hedegård Andersen, Carsten Holst-Jensen, Else Marie Pedersen og Erling Møller Pedersen

Vejleder: Stig Andur Pedersen

86/84 "SECURITY IMPLICATIONS OF ALTERNATIVE DEFENSE OPTIONS FOR WESTERN EUROPE"

PEACE RESEARCH SERIES NO. 2

af Bent Sørensen

87/84 "A SIMPLE MODEL OF AC HOPPING CONDUCTIVITY IN DISORDERED SOLIDS"

af Jeppe C. Dyre

88/84 "RISE, FALL AND RESURRECTION OF INFINITESIMALS"

af Detlef Laugwitz

89/84 "FJERNVARMEOPTIMERING"

af Bjarne Lillethorup & Jacob Mørch Pedersen

90/84 "ENERGI I 1.G- en teori for tilrettelæggelse"

af Albert Chr. Paulsen

91/85 "KVANTETEORI FOR GYMNASIET"
1. Lærervejledning

Projektrapport af: Birger Lundgren, Henning Sten Hansen og John Johansson

Vejleder: Torsten Meyer

92/85 "KVANTETEORI FOR GYMNASIET
2. Materiale

Projektrapport af: Birger Lundgren, Henning Sten Hansen og John Johansson

Vejleder: Torsten Meyer

93/85 "THE SEMIOTICS OF QUANTUM-NON-LOCALITY"
af Peder Voetmann Christiansen

94/85 "TREENIGHEDEN BOURBAKI - generalen, matematikeren og ånden"

Projektrapport af: Morten Blomhøj, Klavs Frisdahl og Frank M. Olsen

Vejleder: Mogens Niss

95/85 "AN ALTERNATIV DEFENSE PLAN FOR WESTERN EUROPE"

Peace research series no. 3

af Bent Sørensen

96/85 "ASPEKTER VED KRAFTVARMEFORSYNING"
af Bjarne Lillethorup

Vejleder: Bent Sørensen

97/85 "ON THE PHYSICS OF A.C. HOPPING CONDUCTIVITY"

Jeppe C. Dyre

98/85 "VALGMULIGHEDER I INFORMATIONSALDEREN"
af Bent Sørensen

99/85 "Der er langt fra Q til R"

Projektrapport af: Niels Jørgensen og Mikael Klintorp
Vejleder: Andur Pedersen

100/85 "TALSYSTEMETS OPBYGNING"

af Mogens Niss

101/85 "EXTENDED MOMENTUM THEORY FOR WINDMILLS IN PERTURBATIVE FORM"

af Ganesh Sengupta

102/85 "OPSTILLING OG ANALYSE AF MATEMATISKE MODELLER, BELYST VED MODELLER OVER KØERS FODEROPTAGELSE OG - OMSÆTNING"

Projektrapport af: Lis Eilertzen, Kirsten Habekost, Lill Røn og Susanne Stender

Vejleder: Klaus Grünbaum

103/85"ØDSLE KOLDKRIGERE & VIDENSKABENS LYSE IDEER"

Projektrapport af: Niels Ole Dam og Kurt Jensen

Vejleder: Bent Sørensen

104/85 "ANALOGREGNEMASKINEN OG LORENZLIGNINGER"

af: Jens Jæger

105/85 "THE FREQUENCY DEPENDENCE OF THE SPECIFIC HEAT AT THE GLASS TRANSITION"

af Tage Christensen

"A SIMPLE MODEL OF AC HOPPING CONDUCTIVITY"

af Jeppe C. Dyre

Contributions to the Third International Conference on the Structure of Non-Crystalline Materials held in Grenoble July 1985

106/85 "QUANTUM THEORY OF EXTENDED PARTICLES"

af Bent Sørensen

107/85 "ÉN MYG GØR INGEN EPIDEMI"

- flodblindhed som eksempel på matematisk modellering af et epidemiologisk problem.

Projektrapport af: Per Hedegård Andersen, Lars Boye, Carsten

Holst Jensen, Else Marie Pedersen og Erling Møller Pedersen
Vejleder: Jesper Larsen

108/85 "APPLICATIONS AND MODELLING IN THE MATHEMATICS CURRICULUM"
- state and trends -
af Mogens Niss

109/85 "COX I STUDIETIDEN"
- Cox's regressionsmodel anvendt på studenteroplysninger fra RUC
Projektrapport af: Mikael Wennerberg Johansen, Poul Kattler og Torben J. Andreasen
Vejleder: Jørgen Larsen

110/85 " PLANNING FOR SECURITY "

af Bent Sørensen

111/85 "JORDEN RUNDT PÅ FLADE KORT"
Projektrapport af: Birgit Andresen, Beatriz Quinones og Jimmy Staal
Vejleder: Mogens Niss

112/85 "VIDENSKABELIGGØRELSE AF DANSK TEKNOLOGISK INNOVATION FREM TIL 1950 - BELYST VED EKSEMPLER"
Projektrapport af: Erik Odgaard Gade, Hans Hedal, Frank C. Ludvigsen, Annette Post Nielsen og Finn Physant.
Vejleder: Claus Bryld og Bent C. Jørgensen

113/85 "DESUSPENSION OF SPLITTING ELLIPTIC SYMBOLS II"
Af: Bernhelm Booss og Krzysztof Wojciechowski

114/85 "ANVENDELSE AF GRAFISKE METODER TIL ANALYSE AF KONTIGENSTABELLER"
Projektrapport af: Lone Biilmann, Ole R. Jensen og Anne-Lise von Moos
Vejleder: Jørgen Larsen

115/85 "MATEMATIKKENS UDVIKLING OP TIL RENÆSSANCEN"
af: Mogens Niss