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Connection between the Meyer-Neldel rule and stretched-exponential relaxation

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We demonstrate that the key element for a thermally activated process to follow the stretched-exponential relaxation and the Meyer-Neldel rule is the exponential energy distribution of defect traps. We point out that the characteristic temperature associated with the exponential energy distribution obtained from the stretched-exponential relaxation and the Meyer-Neldel rule should have the same value. This criterion provides a very good test for the underlying mechanism as proposed. The model is applied to the data in semi-insulating GaAs. We show that the decay of the persistent photoconductivity of the studied material after different illumination time follows the stretched-exponential relaxation. The obtained characteristic temperature $T_0=453$ K is in excellent agreement with that from the Meyer-Neldel rule for the dc conductivity measurement. The model is also successfully confirmed by the data in hydrogenated amorphous silicon.

In this paper we establish a link between two characteristic phenomena of solids. These phenomena are the stretched-exponential relaxation that describes the relaxation of a physical quantity toward equilibrium, and the Meyer-Neldel (MN) rule that describes an exponential relation between the activation energy and the preexponential factor. The MN rule has been observed in a wide variety of materials. These include single-crystal,[1] polycrystalline,[2] amorphous,[3] and organic solids,[4] and even ionically conducting crystals and glasses.[5] The expression of the MN rule for the dc conductivity can be written as[6]

$$\sigma=\sigma_{00}e^{E_\tau/kT_0}e^{-E_\tau/kT}, \tag{1}$$

where σ_{00} and T_0 are constants within a class of related materials, and E_τ is the activation energy. Although the MN rule is similar in a variety of materials suggesting a common underlying mechanism, its origin is unclear. Recently, several interesting models have been proposed to derive the MN rule. For example, Jackson[7] found that whenever a multiple-trapping transport process is observed over fixed distances as a function of temperature, a MN rule should be observed for this transport quantity. Dyre[8] and Crandall[9] used an exponential probability distribution of energy barriers to obtain the MN rule. For most of the people the MN rule is often associated with disorder of some form within the material.

The stretched-exponential relaxation of a physical quantity N is described by the time dependence[10]

$$N(t)=N(0)\exp[-(t/\tau)^\alpha], \tag{2}$$

where τ is the relaxation time, and $0\leq\alpha\leq 1$. It has also been observed in a wide class of materials including crystalline[11] and amorphous[12] solids. Its physical mechanism is also not clearly established. Campos, Giacometti, and Silver[13] and Crandall[9] used an exponential distribution of traps to derive this expression. Kakalios, Street, and Jackson[12] attributed this relaxation to dispersive transport characterized by a power-law time decay of the mobility or diffusion.

Reviewing the previous derivations for the stretched-exponential relaxation and the MN rule, we can find that some of the assumptions for these two characteristic phenomena are similar. For example, Kakalios, Street, and Jackson[12] and Jackson[7] both assumed dispersive transport characterized by a power-law time dependence to obtain the stretched-exponential relaxation and the MN rule, respectively. Also it is known that the dispersive transport is a consequence of an exponential energy distribution of traps. Thus, one should be able to derive both the stretched-exponential relaxation and the MN rule from a common origin which is the exponential energy distribution. However, this point was not firmly established by the previous authors. Jackson[7] has derived these two expressions, but the physical system is limited to a multiple-trapping transport process over fixed distances. Crandall[9] went further to obtain the results by using an exponential distribution of activation barriers, but the discussed phenomenon is restricted to the Staebler-Wronski effect in hydrogenated amorphous silicon, and the connection between the stretched-exponential decay and the MN rule was not tested.

This paper demonstrates that the key element for a thermally activated process to obey the stretched-exponential relaxation and the MN rule is the exponential energy distribution of defect traps. This result is first derived by considering the relaxation of the stored charge carriers in a semiconducting material. We point out that the characteristic temperature associated with the exponential energy distribution of traps obtained from the stretched-exponential relaxation and the MN rule should have the same value. This criterion provides a very good test for underlying mechanism as we proposed. The connection between the stretched-exponential relaxation and the MN rule is then further investigated by considering the data in semi-insulating GaAs and hydrogenated amorphous silicon.

Let us first consider a semiconducting material containing deep traps which may be a result of the presence of impurities or lattice imperfections. We want to calculate the relaxation of the stored charge carriers in the deep traps and the variation of the dc conductivity with the ac-

tivation energy when the number of deep defects is changed. Here our derivation is similar to the procedures given by Crandall.[9] The assumptions made in our model are as follows: (1) the trap distribution is given by

$$n_t(E)=\frac{N_t}{kT_0}\exp(E'/kT_0)\,, \tag{3}$$

where $n_t(E)$ is the density of traps per unit energy, T_0 characterizes the width of the distribution, N_t is the total number of the traps, and $E'=E-E_h$, where E_h is the highest energy barrier for the stored charge carriers to relax from the traps. (2) The cross section of the traps are assumed to be independent of energy so that the probability for the occupation of the stored charge carrier in a trap is proportional to $n_t(E)$.

The exponential energy distribution of defects is well known. It has been used to describe the various behaviors in disorder solids. A brief review of the history of the exponential energy distribution has been given by Macdonald.[14] It has also been applied to the defects in crystalline solids.[13] The applicability of the exponential energy distribution to deep traps in disorder solids as well as in crystalline solids can be understood by the Dyre's argument.[8] At T_0, the relevant lattice degrees of freedom freeze, so that the defects for $T\leq T_0$ are unable to exchange energy with the lattice. When the lattice freezes, the defect-lattice interaction energy E' becomes a function of the defect coordinates only. This function is random in space and Eq. (3) just expresses the probability of finding energy E' at a given defect position. Thus, Eq. (3) is a consequence of a frustration of thermal equilibrium at T_0. The frustration takes place on cooling at the sample preparation, and it reflects the property of the freezing of thermal disorder of defects at T_0. As long as defects are present, the frustration should exist which does not depend on whether the material is disorder or crystalline. The concept here is not new. In 1950, Busch[15] suggested that a freezing of the donor concentration during cooling after the sample preparation may exist in extrinsic semiconductors. Equation (3) represents the trap density increases with the energy barrier for the relaxation of stored charged carriers. In principle, trap distributions could be exponentially increasing or decreasing functions of the energy barrier. As we point out later, these two distributions will lead to differences in the relaxation behavior. Here, we will restrict ourselves to Eq. (3).

The relaxation of charge carriers from deep traps is generally a thermal process. For a thermally activated process, the transition rate is

$$R=R_0e^{-E/kT}\,. \tag{4}$$

The rate of change of deep traps having charge carriers is

$$\frac{dN_t(t)}{dt}=-\int_{E_l}^{E_h}n_t(E)R(E)dE\,, \tag{5}$$

where E_l is the minimum observable transition energy for the relaxation.

$$E_l=kT\ln(\nu_0 t)\,, \tag{6}$$

where ν_0 is the attempt frequency. The states with the energy barrier lower than E_l will remain in equilibrium throughout the time of measurement, and their change cannot be observed. Using the assumed distribution functions, Eq. (5) becomes

$$\frac{dN_t(t)}{dt}=-\frac{N(t)}{kT_0}\int_{E_l}^{E_h}R_0e^{-E/kT}e^{(E-E_h)/kT_0}dE\,. \tag{7}$$

Since we are interested in the range of temperature less than T_0, the argument of the integral decreases exponentially at higher energy. Thus the lower limit dominates the integral. The integration in Eq. (7) gives

$$\frac{dN_t(t)}{dt}=-\frac{N(t)}{kT_0b}R_0e^{-E_h/kT_0}e^{-bE_l}\,, \tag{8}$$

where $b=1/kT-1/kT_0$. Substituting Eq. (8), we obtain

$$\frac{dN_t(t)}{dt}=-\frac{N(t)}{kT_0b}R_0e^{-E_h/kT_0}(\nu_0 t)^{\alpha-1}\,, \tag{9}$$

where $\alpha=T/T_0$. From this equation, we can see immediately that the dispersive transport characterized by a power-law time dependence is just the consequence of the exponential energy distribution. The solution of the stored charge carriers remaining in the traps as a function of time is then

$$N(t)=N(0)e^{-(t/\tau)^{\alpha}}\,, \tag{10}$$

where

$$\tau=\nu_0^{-1}e^{E_\tau/kT}\,, \tag{11}$$

and E_τ is given by

$$E_\tau=kT_0\ln(\nu_0)+kT_0\ln(1-\alpha)-kT_0\times\ln(R_0e^{-(E_h/kT_0)})\,, \tag{12}$$

τ is the average relaxation time for the stored charge carriers, E_τ is the average thermal activation energy for this relaxation. Equation (10) shows that the relaxation of the stored charge carriers in the traps follow a stretched-exponential function, and Eq. (12) is just the MN rule connecting E_τ to the logarithm of ν_0. The average relaxation time as a function of the activation energy shown in Eqs. (11) and (12) is exactly the same as the expression obtained by Dyre[8] and Crandall.[9] The physical processes under discussion, however, are very different. We consider the relaxation of the stored charge carriers in the traps, while Dyre[8] considered the hopping of localized charge carriers. But, this result should not be surprising. As long as the processes are thermally activated and the involved defects have an exponential energy distribution, the average relaxation time should follow the expression as shown above.[8,9] Thus, any physical quantities which are inversely proportional to the average relaxation time should have its proexponential factor depending exponentially on the activation energy. For example, the dc conductivity σ in solids can thus be written as

$$\sigma=\sigma_{00}e^{E_\tau/kT_0}e^{-E_\tau/kT}\,, \tag{13}$$

where σ_{00} is a constant within a class of related materials. This expression is just the familiar formula of the MN rule as shown in Eq. (1). We thus demonstrate that the key element for a thermally activated process to follow the stretched-exponential function and the MN rule is the ex-

ponential energy distribution of defects. Even the physical system discussed here is the relaxation of the stored charge carriers from traps, the results can be applied to the relaxation of an arbitrary physical quantity as long as the defects involved in the process have an exponential energy distribution and the process is thermally activated, for example, the relaxation of band-tail carriers in hydrogenated amorphous silicon studied by Kakalios, Street, and Jackson.[12]

According to the thermodynamic model by Bar-Yam, Adler, and Joannopolus,[16] it predicts that all defect distributions in a material are determined by the same characteristic temperature T_0.[9] Thus, the characteristic temperature obtained from the stretched-exponential relaxation and the MN rule should be the same for a material even if these two phenomena are caused by different defects. This is a very important criterion to test the underlying mechanism for the two expressions we proposed above.

Equations (10) and (12) can now be quantitatively compared with the experimental data. Jimenez *et al.*[17] observed an optically induced long-lifetime photoconductivity in semi-insulating bulk GaAs. This result is explained by the fact that there are deep traps existing in GaAs which can trap photoelectrons and leave photoholes remaining a long time delocalized in the valence band before they recombine with the electrons releasing from the traps. Thus, the relaxation of this persistent photoconductivity is equivalent to the relaxation of the stored charge carriers from the traps as discussed above. According to our discussion, if the traps are an exponential energy distribution, the relaxation should follow a stretched-exponential function. In Fig. 1 we plot $\ln[\ln I(0) - \ln I(t)]$ vs $\ln t$ for the experimental data obtained at 77 K for different illumination time. The linear behaviors for all of these plots are evident, which indicates that the decay of the photoexcited charge carriers can be described by the stretched-exponential function. The decay exponents α for all of these plots are about 0.17 ± 0.01, which corresponds to the characteristic temperature $T_0 = 453 \pm 25$ K.

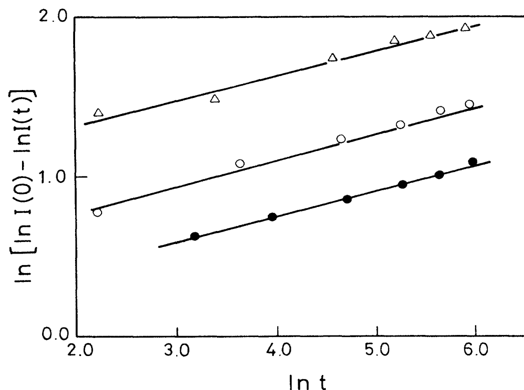

FIG. 1. Plots of $\ln[\ln I(0) - \ln I(t)]$ vs $\ln t$ for the photocurrent decays in semi-insulating GaAs at 77 K after several different periods of illumination time T_i with 1.13-eV photons. Solid dots, open circles, and triangles represent $T_i = 5$, 9.5, and 10.5 min, respectively. The units of time for all the plots are in seconds.

The decay of persistent photoconductivity in crystalline semiconductors following a stretched-exponential function is not new, a fact that has been observed previously.[11,18] However, the mechanism of the decay kinetics has not yet been established. Here, we point out that the exponential energy distribution of the trap density may play an important role to determine the relaxation of the photoexcited charge carriers.

Let us now consider the justification of using Eq. (3). This equation shows that the trap density increases with the energy barrier for the relaxation of stored charge carriers. Because of the exponential distribution of states, the number of charge carriers stored in the traps with high-energy barriers increases rapidly with illumination time. This implies that longer illumination time will produce a persistent photoconductivity that is harder to relax. If, in contrast, there were more traps with low-energy barriers, longer illumination would not produce an observable number of stored carriers that are harder to relax. Thus, the activation energy for the annealing of the persistent photoconductivity should depend on illumination time. This result is just what has been observed in Ref. 17. In the model of dispersive transport,[7] the activation energy is written as

$$E_\tau = kT_0 \ln(\nu_0) + kT_0 \ln\left[\frac{\alpha}{AD_{00}}\right], \tag{14}$$

where A is a constant and D_{00} is a microscopic diffusion coefficient. Because this expression does not contain a term equivalent to E_h, E_τ does not depend on illumination time. This model predicts a single annealing energy of all metastable states because the initial distribution of transport agents in their dispersive trapping sites is independent of the illumination time.[9] However, as shown in Ref. 17, the annealing time clearly depends on the illumination time, which favors the present discussion.

The MN rule in semi-insulating GaAs has been observed by Hilsum.[1] The calculated value of the characteristic temperature is found to be 457 K which is in excellent agreement with the T_0 obtained from the stretched-exponential relaxation of the persistent photoconductivity in semi-insulating GaAs as discussed above. Considering the rather different experimental measurements by those authors, the agreement is surprising. This agreement may indicate that the mechanism for the stretched-exponential relaxation and the MN rule as proposed above are indeed correct.

As a further test of the connection between the stretched-exponential relaxation and the MN rule, consider the experimental results in hydrogenated amorphous silicon. Kakalios, Street, and Jackson[12] showed that the relaxation of the band-tail carriers obeys the stretched-exponential function with a characteristic temperature 600 K. This value is in excellent agreement with that obtained from the MN rule in hydrogenated amorphous silicon as shown in Fig. 1 of Ref. 7. In addition, several experiments show more than one annealing energy for metastable defects[9] in the same sample which also justifies the validity of Eq. (3).

In summary, we have demonstrated that the key element leads a thermally activated process to follow the

stretched-exponential relaxation and the MN rule is the exponential distribution of defect traps. We point out that the characteristic temperature obtained from the stretched-exponential function and the MN rule should have the same value. This criterion provides a very good test for the underlying mechanism as we proposed. The connection between the stretched-exponential relaxation and the MN rule has been successfully confirmed by the experimental results in semi-insulating GaAs as well as in hydrogenated amorphous silicon. Thus, this paper not only establishes the close connection between these two characteristic phenomena in solids, but also demonstrates a microscopic mechanism for them. The distinction between the present discussion and the model of dispersive transport lies in the observed dependence of annealing time upon illumination time which leads to the difference in the annealing energy, a result which favors the present discussion. However, based on different assumptions, these models can both predict the stretched-exponential relaxation and the MN rule. This is because they both reflect the underlying disorder of solids.

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