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Origin and consequences of the compensation (Meyer-Neldel) law

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We have recently demonstrated that the Meyer-Neldel (MN) rule (compensation law) may be understood as arising naturally when the activation energy for a process is significantly larger than both the typical excitations available and kT. This conclusion was supported by the results of two microscopic models, related to special cases. In the present paper we present arguments, based on general results from statistical physics, which lead to the same conclusion. We show that this simple explanation also leads to the solution of a number of puzzles which have been associated with Meyer-Neldel behavior. We show that phenomena in groups of similar materials yield similar MN slopes. Finally, we show that the values of the slope for semiconductors with gaps in the 1–2-eV range are consistent with the suggestion that optical phonons are the source of the excitation energy in such processes.

I. INTRODUCTION

The compensation law, or Meyer-Neldel (MN) rule, has been known as an empirical result since 1937.[1] This law is obeyed by many processes[2,3] including annealing phenomena[4,5] and electronic processes[6] in amorphous semiconductors, trapping in crystalline semiconductors,[7] conductivity in ionic conductors,[8–10] aging of insulating polymers,[11] biological death rates,[12] and chemical reactions.[13] An equivalent formulation, the isokinetic rule, has been known to chemists since 1929.[14]

The MN rule describes groups of related activated processes for which a measured property X is given by

$$X = X_0 e^{-\Delta/kT} . \tag{1}$$

When Δ varies, X_0 obeys the equation

$$\ln X_0 = a + b\Delta . \tag{2}$$

Here a and b are positive constants and k is the Boltzmann constant. In what follows, we shall concern ourselves primarily with the value of the slope b. However, instead of considering values for b, we shall treat the values of b^{-1}, a characteristic energy, which we shall call Δ_0. The isokinetic rule states[13,14] that the various extrapolated Arrhenius plots cross at a temperature T_0, the isokinetic temperature. It is clear from Eqs. (1) and (2) that $kT_0 = \Delta_0$.

Numerous microscopic models for the origin of the MN rule in particular systems have been proposed as applying only to the system in question. These models have generally been based on a one-phonon activated process (that is, assuming that the Miller-Abrahams approximation[15] applies) with a distribution of densities of initial and final states leading to Eq. (2). This generally signifies[16] an exponential density of states. Crandall has shown[5] that such models, which we shall call "density-of-states models" in what follows, are not unique, in that several mechanisms could lead to the same result. We believe, however, that more fundamental objections can be raised to these models.

First, if exponential densities of states are necessary for the MN rule to apply, it is difficult to understand why it should be so widespread. In particular, it is difficult to understand why it should apply to crystalline materials[7,8,10] for which such distributions would not be expected to be appropriate. Second, it is not clear from such explanations why the MN rule should apply only for large values of Δ. An example of the deviation from the MN rule is shown in Fig. 1. For the conductivity of ionic crystals, 0.9 eV is apparently a "small" value of Δ, below which the MN rule breaks down. In Fig. 2 we see that the dependence of the prefactor on activation energy is small, and in the wrong direction, for substituted β-aluminas for which the activation energy is below 0.3 eV. The MN rule is also known to apply to deep traps in crystalline semiconductors, as discussed in Sec. III, but not to shallow donors.[17] The size of Δ for which the MN rule fails is apparently different for different systems. This is also discussed in Sec. III.

A third difficulty with the density-of-states models is that if we calculate attempt frequencies for various phenomena, such as metastable defect annealing[4,5] or electron hopping[18] in amorphous silicon, we frequently find values much larger than 10^{12} or 10^{13} Hz, which is physically unreasonable. We shall show below that entropy terms, which may vary by many orders of magnitude, need to be included in the prefactor. This readily explains the wide variation of the prefactor.

Finally, it is difficult to understand from these models

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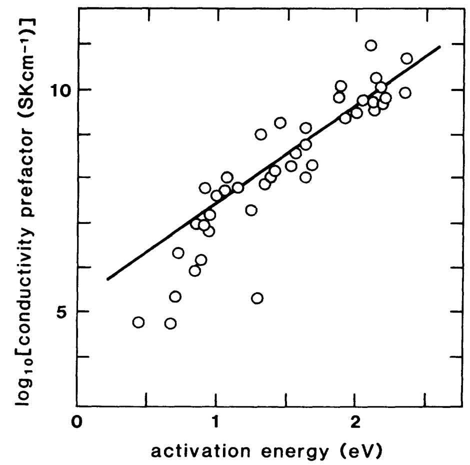

FIG. 1. Log_{10} conductivity prefactor vs activation energy for 42 ionic crystals. These are primarily "alkali-halide-type" crystals. The solid line represents the MN law (after Ref. 8. Primary references are given in Ref. 8.)

why totally different phenomena in the same material should exhibit the same value of Δ_0, as we shall discuss below, or why different but related materials should exhibit about the same value of Δ_0 and fall on the same MN plot. Figure 1 shows a case of this kind, and we shall treat others below.

We believe that the reason for these problems has been the assumption, explicit or implicit, that the excitation process involves only one phonon. In contrast, it has long been known that many phonons must be involved both in trapping and detrapping of electrons, either by cascade[19] or by multiphonon[20] processes.

In the following section, we develop general thermodynamic arguments in support of a model (hereafter called YM for Yelon and Movaghar), which resolves all of these difficulties. This model was previously presented in Ref. 3 along with specific physical examples. We shall demonstrate that this model predicts the MN rule, with slight modification in the detailed form. We also describe characteristics of systems for which deviations from the MN rule are expected. In Sec. III we consider the consequences of the MN rule as understood in light of the new model. We examine experimental results for Δ_0 in order to compare them among themselves. We also compare the results with predictions for those cases for which microscopic calculations exist, that is, for acoustic- or optical-phonon-assisted electron hopping. Finally, in Sec. IV, we present our conclusions.

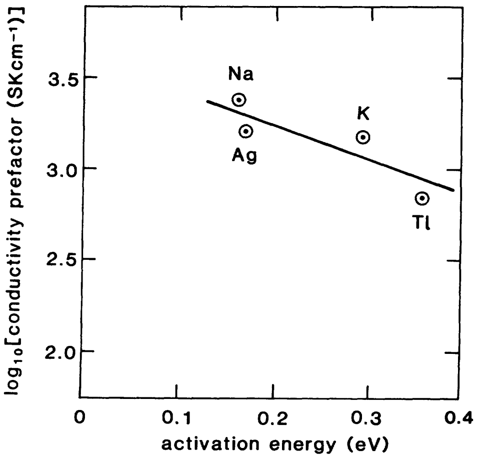

FIG. 2. Log_{10} conductivity prefactor vs activation energy for a series of β-aluminas substituted with the elements indicated (from Ref. 9).

II. ORIGIN OF THE MN RULE

The approach taken here may be seen as a generalization of the phenomenological approach taken by many authors,[9,21,22] who consider, as in the Eyring theory,[23] that in a reaction the rate is equal to $\nu_{00}e^{-\delta G/kT}$, where δG is the difference between the free energy of the state at the peak of an activation barrier and that of the initial state and ν_{00} is a constant. Since

$$\delta G = \delta H - T\delta S \ , \tag{3}$$

it is evident that

$$\nu = \nu_{00} e^{\delta S/k} e^{-\delta H/kT} \ . \tag{4}$$

Thus, the compensation law of Eq. (2) follows if the activation entropy is proportional to the activation enthalpy. This is not the case when the activation enthalpy, or energy, is small. In that case, a single excitation dominates the process and the reaction is isoentropic. If the excitation is a phonon, the Miller-Abrahams approximation applies.

However, as described in YM, if the activation energy is large compared to typical excitations of the system, it becomes necessary to assemble many excitations for the reaction to take place. As the entropy is proportional to the logarithm of the number of different ways of assembling these excitations, δS will increase as δH increases. The MN rule will follow if the two are proportional to each other. That this will be approximately true may be shown on quite general grounds of statistical thermodynamics.

As a first example, we assume that the energy to surmount the enthalpy barrier to a physical process δH is obtained from multiphonon annihilation. In a simple Einstein model of the phonon spectrum, with each quantum having energy E_E, $n = \delta H/E_E$ phonons must be annihilated in the excitation. Assuming N phonons lie within the interaction volume from which they can be annihilated, the dimensionless entropy change associated with the excitation over the barrier is the natural logarithm of the number of ways of assembling n out of N interacting phonons. Thus

$$\delta S/k = \ln\left[\frac{N!}{n!(N-n)!}\right]$$

$$\approx N\ln\left[\frac{N}{N-n}\right] + n\ln\left[\frac{N-n}{n}\right] \ , \tag{5}$$

where the second expression is obtained from the application of Stirling's approximation. For $n \ll N$,

$$\delta S/k \approx n \ln\frac{N}{n} \approx \frac{\delta H}{E_E}\ln N \tag{6}$$

and the desired proportionality of the changes in entropy and enthalpy is obtained. Combining Eqs. (4) and (6) yields

$$\nu = \nu_{00} e^{\delta H(\ln N)/E_E} e^{-\delta H/kT} . \tag{7}$$

If N is independent of δH, we obtain exactly the MN rule with $\Delta_0 = E_E/\ln N$. If not, there is a logarithmic correction. We note further that this result does not apply when $\delta H \leq E_E$.

Let us next examine the contribution to δS of assembling and annihilating other types of excitations. Consider a volume of interaction V within which an effective coupling exists between a particle and the surrounding bath. The density of states (the totality of configurations with energy ϵ within V) is given by

$$\tau(\epsilon) = \exp[S(\epsilon)] , \tag{8}$$

where S is the total entropy within the volume V.

We integrate $1/T = dS(\epsilon)/d\epsilon$ to obtain $\epsilon - \epsilon_0 = \int T\, dS$, where ϵ_0 is the zero-point energy. For example, for acoustic phonons in the Debye approximation $S \propto T^3$, giving rise to an energy dependence,

$$\tau(\epsilon) \propto \exp[(\Delta/\Delta_p)^{3/4}] , \tag{9}$$

where

$$\Delta = \epsilon - \epsilon_0 .$$

Electrons have $S \propto T$, so that

$$\tau(\epsilon) \propto \exp([\Delta/\Delta_e]^{1/2}) . \tag{10}$$

These relations tell us how the entropy, and therefore, the number of ways of assembling excitations within V varies with the total energy ϵ. It is interesting that for the "normal excitations" for which $S \propto T^\beta$ and $\beta > 0$, the density of states has the form $\exp([\Delta/\Delta_0]^\alpha)$, where $0 \leq \alpha \leq 1$. The meaning of the constants such as Δ_p and Δ_e is, of course, different for each model considered.

When the transition rate to the excited state is determined by the time it takes for the particle to find a suitably "hot" region in the system and annihilate excitations with a total energy $\epsilon - \epsilon_0 = \delta H$,

$$\delta S \sim k \ln\tau(\epsilon) \sim \left[\frac{\delta H}{\Delta_0}\right]^\alpha . \tag{11}$$

For acoustic phonons,

$$\delta S \sim \left[\frac{\delta H}{\Delta_p}\right]^{3/4} , \tag{12}$$

and for electrons,

$$\delta S \sim \left[\frac{\delta H}{\Delta_e}\right]^{1/2} . \tag{13}$$

This simple thermodynamic argument illustrates the universality of the result. The magnitude of the effective interaction volume is somewhat vague. However, simple considerations suggest that this should be of order $(l_{\text{in}})^d$, where l_{in} is the characteristic interaction length and d is the dimensionality of the volume in which the interaction takes place. If l_{in} varies with δH, the expressions above must be corrected slightly. If the transitions are between localized states, V should be the volume over which the hotspot can find a particle to excite.

The possibility of values of α different from 1 is not of great concern, as pointed out by YM, as it is notoriously difficult[24] to prove which value of α gives the best straight-line fit to data. That is, data which have always been treated as fitting $\alpha = 1$ may, in fact, fit another value better. However, as we shall discuss below, $\alpha = 1$ is probably appropriate for many situations.

If we wish to obtain predictions for values of Δ_0, or to obtain reliable values of corrections of α, we need microscopic models, of course. The only such models which have been developed in sufficient detail to permit exact calculations of multiexcitation effects, of which we are aware, are two models of phonon-assisted electron hopping due to Emin.[25] As these have been discussed in detail in YM, we present only the results here. When Δ is small compared with the phonon energies, Emin obtains the Miller-Abrahams approximation, as expected. However, when Δ is large, it appears in an exponential in the prefactor. For optical phonons,[3] this prefactor is

$$\exp\left[\frac{\Delta}{\hbar\omega_0}\right]\ln\left[\frac{2E_b}{\hbar\omega_0}\right] , \tag{14a}$$

where ω_0 is the optical-phonon frequency and E_b describes the strength of the local electron-phonon coupling ($E_b \gg \hbar\omega_0$). That is, $\delta S/k$ contains a term of the form

$$\frac{\delta H}{\hbar\omega_0}\ln\left[\frac{2E_b}{\hbar\omega_0}\right] . \tag{14b}$$

If we identify E_E with $\hbar\omega_0$ and compare Eqs. (6) and (14b), we see that they are quite similar, differing only in the form of the logarithmic correction. In fact, it is clear that the N of Eq. (6) should vary monotonically with the ratio of the coupling strength to the phonon energy.

For acoustic phonons,[3] the prefactor contains a term $\exp[(\Delta/\Delta_0)^{2/3}]$ where

$$\Delta_0 = \tfrac{2}{9}\gamma^{-1/2}\hbar\omega_D , \tag{15a}$$

where γ is an electron-phonon coupling constant and ω_D is the Debye frequency. Thus $\delta S/k$ contains a term of the form

$$\left[\frac{\delta H}{\Delta_0}\right]^{2/3} . \tag{15b}$$

This result is not very different from Eq. (10), which was obtained by considering only the number of available acoustic phonons.

Thus, we see that both the general and specific models yield predictions which approximate the MN rule, when

δH is sufficiently large. We thus conclude that the MN rule is to be expected whenever such circumstances are encountered. This conclusion, that compensation arises from multiexcitation processes, has previously been reached by Khait[26] based on a kinetic many-body theory of short-lived energy fluctuations. While the two theories are, in a sense, equivalent, we believe that the present approach is more convenient and more readily understood.

III. CONSEQUENCES OF THE MN RULE: COMPARISON WITH EXPERIMENT

It is clear that the model described above resolves the first two difficulties discussed in the Introduction. It follows directly from our discussion that the MN rule will be widespread, since it should occur whenever δH is large compared to the excitations supplying the enthalpy. Clearly, it should apply equally well to crystalline and to amorphous materials. We also predict that it will not apply at low activation energies, as shown in Figs. 1 and 2.

It is also clear that the third difficulty, the unreasonable values of attempt frequencies, is also resolved by this model. This is most readily seen by referring to Eq. (7), which may be taken as an example. The quantity which would, in the density-of-states models, not be very different from the attempt frequency ν_{00} is, in fact, $\nu_{00}e^{\delta H \ln N/E_E}$. Thus, the exponential can greatly increase the apparent attempt frequency, yielding values much larger than phonon frequencies (there is no reason why the true attempt frequency ν_{00} may not be less than a phonon frequency).

Since the existence of the MN rule and its detailed form arise from the fact that energy is being extracted from a particular reservoir, it is clear, in principle, why different phenomena for the same material should show the same MN slope, if the source of the energy is the same. To consider this further, it is helpful to examine the experimental situation.

At some future time, it may be appropriate to compare detailed predictions for the prefactor with accurate experiments. In a similar vein, it may eventually be of interest to experimentally determine the value of α, the power to which Δ/Δ_0 appears in the exponent of the prefactor. Our ambitions in what follows are considerably more modest. Here, we shall assume that the classical MN rule is appropriate, that is, $\alpha=1$, and no correction factors are needed. Thus, the only quantity which we shall consider is Δ_0.

Perhaps the best available example of a material for which many different experiments obey the MN rule is amorphous hydrogenated silicon, *a*-Si:H. Crandall has shown[5] that many experiments on the annealing of various metastable defects in this material, doped and undoped, fit a MN plot. This includes several experiments in which two different activation energies are observed for the same sample. The data from 15 different samples are shown in Fig. 3, in which the apparent attempt frequency is plotted against activation energy. The value of Δ_0 obtained from this figure is about 40 meV.

Many electronic phenomena in *a*-Si:H also obey the MN rule.[6,27] These include conductivity of undoped, doped, and light-soaked material, field-effect, and space-charge-limited currents. While it is easy to understand, from the preceding discussion, why hopping conductivity should show compensation, it may appear surprising that the model presented in Sec. II applies equally well to dc conductivity when electrons are excited above the mobility edge. We shall show elsewhere that this occurs for systems which exhibit both strong electron-phonon coupling and localization. The effective one-electron density of conducting states then includes phonon contributions similar to those treated in Sec. II. That is, multiexcitation effects contribute to the effective density of states.

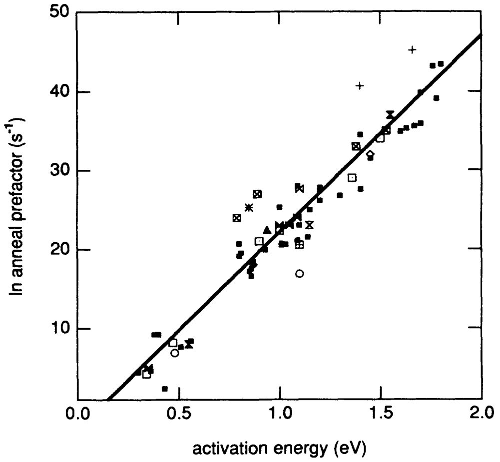

FIG. 3. ln annealing prefactor vs activation energy for a number of annealing experiments on *a*-Si:H. (After Ref. 5. The various symbols refer to primary references given in Ref. 5.)

These electronic experiments on *a*-Si:H all yield values of Δ_0 between 35 and 55 meV, with the majority clustered about 40 meV. The value of Δ_0 is, to a first approximation at least, the same as for the annealing experiments summarized in Fig. 3. This suggests strongly that the source of energy, and perhaps the mechanism of energy transfer, are the same for all of these activated processes. Possible identification of this source will be discussed below.

Chen and Chang[28] (hereafter referred to as CC) have pointed out that considerable data on deep trapping cross sections (σ_e) in crystalline semiconductors show MN behavior. In Fig. 4, we show the MN plot for crystalline Si (*c*-Si), compiled from two sources.[29] This yields a Δ_0 of 50±25 meV. The capture cross sections σ, displayed in Fig. 4, are all derived from deep-level transient spectroscopy (DLTS) emission measurements. Consequently, they are relevant to the present discussion of excitation out of a localized state.[30]

For GaAs (Ref. 31) and for InP (Ref. 32) which had earlier been shown[7] to obey the MN rule, CC find values of 70 and 60 meV, respectively. We note that all of these crystalline semiconductors show values of Δ_0 which are not very far from that of *a*-Si:H. We suggest that any semiconductors with 1–2-eV gaps will have similar values of Δ_0, as they will obtain their excitation energy from baths, and through interactions, with similar characteristics. What these baths and interactions might

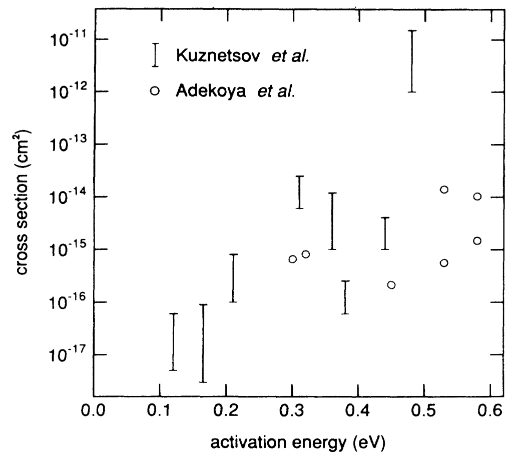

FIG. 4. Log_{10} capture cross section vs trap depth for radiation- and implantation-induced defects in n-type c-Si. The cross section is determined from DLTS emission data of Ref. 29.

be will be discussed below.

If this proposal is correct, it permits us to understand the remarkable results of Coutts and Pearsall,[33] who studied the reverse saturation current in 23 solar cells of 11 categories, made of different materials, with different types of junctions and of contacts. These include Schottky, metal-insulator-semiconductor, homojunction, and heterojunction cells fabricated from CdS/InP, CdS/Cu_xS, Si, CdSe, and single-crystal and polycrystalline InP. Their MN plot is shown in Fig. 5. It again gives a Δ_0 close to 40 meV. Of course, all these solar-cell materials are 1–2-eV band-gap semiconductors.

Not all classes of materials give values of Δ_0 in this range. Figure 1, which is a compilation of many ionic crystals, yields a Δ_0 of 175 meV. Ionic diffusion in such materials, in superionic conductors, and in various glasses yield values[8–10] which range from 150–200 meV. We noted above that the MN rule appears to break down at considerably higher values of δH in these materials then in semiconductors. We may speculate that this is associated with the larger values of Δ_0.

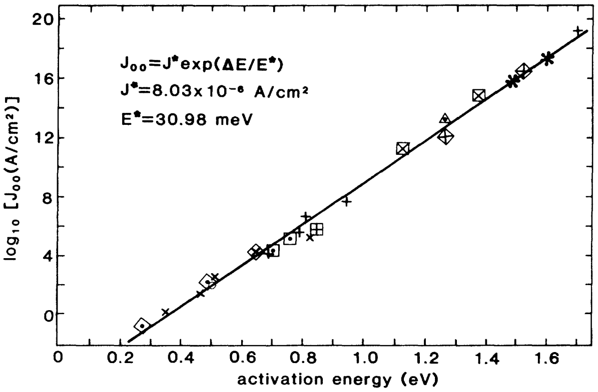

FIG. 5. Log_{10} current prefactor vs activation energy for reverse saturation current in various solar cells. The inset gives fit parameters of the MN rule line (from Ref. 33. The various symbols refer to cell types given in Ref. 33.)

A number of polymer relaxations yield[11,34] values of Δ_0 between 30 and 60 meV. Again, we believe that the existence of a small range of values for a given system indicates a similar source for the activation energy. The thermal killing rates of certain viruses, bacteria, and yeast yield values of 230 meV, comparable to Δ_0 for thermal denaturation of proteins.[12] In contrast, values of Δ_0 for chemical reactions appear to range widely[13] from about 10 to about 160 meV. For arbitrary conditions, the present theoretical situation, as discussed in the preceding section, does not permit us to decide what the excitation bath and coupling mechanism might be.

However, for emission from traps in crystalline semiconductors, it is worthwhile to compare the experimental values with predictions derived from the Emin models. CC have pointed out that, for c-Si, the parameters which are necessary to predict Δ_0 are generally known.[35] For acoustic phonons, using Eq. (15), one obtains a value of 0.75 meV. This is far from the value of 50 meV obtained from Fig. 4. In order to apply Eq. (14), we need values of the average optical-phonon energy for c-Si, which is known[36] to be about 56 meV, and of the coupling energy E_b, which is not known. However, to obtain appropriate values of Δ_0, we need a value of $2E_b/\hbar\omega_0$ near 3, which seems entirely plausible.

GaAs and InP yield values of Δ_0 of 70 and 60 meV, respectively. Since the optical-phonon energies for these two materials are about 36 and 41 meV, respectively,[36] coupling to an optical-phonon bath seems to be a plausible mechanism for these two cases as well. However, the necessary values of $2E_b/\hbar\omega_0$, 1.7 and 2.0 respectively, do not satisfy the approximation $E_b \gg \hbar\omega_0$ that permitted Emin to obtain the result [Eq. (14a)] employed here.

We believe that the agreement between the experimental value and the Emin model suggests that the optical-phonon bath is the source, or sink, for the necessary excitations. Intuitively, we would expect coupling with optical phonons to be a more likely mechanism for producing large excitations than would coupling with acoustic phonons, as fewer of them would be needed.[37] Thus $\alpha=1$ should frequently be appropriate.

We speculate that the similarity of the values of Δ_0 for all the semiconductors above suggests that in all of these cases, including a-Si:H, which has "optical" phonons at energies similar to those for c-Si, it is the optical phonons which provide the energy bath for the excitation. It may also be that the electron-phonon interaction is the coupling mechanism, as we would expect that Δ_0 would not be very sensitive to the coupling strength E_b, since it appears only as a logarithmic correction to Δ_0 [see Eq. (14)].

IV. CONCLUSIONS

We have shown that the MN rule arises naturally in situations in which the activation energy for a process is considerably larger than both kT and the typical excitations of the system. This model explains why the MN rule is so ubiquitous among "high" activation-energy processes, why it is not observed for "low" activation energy, and why diverse phenomena in the same material exhibit the same inverse MN slope Δ_0. It also offers a simple explanation of why similar materials show roughly the same value of Δ_0. We have presented experimental evidence from the literature in support of the model; the experimental situation confirms our general picture.

In order to compare theoretical and experimental values of Δ_0, it is necessary to have detailed microscopic models. We have such a model only for the case of phonon-assisted electron hopping. Some experiments with semiconductors suggest that this model yields realistic values for these materials. Values of Δ_0 for other materials may be quite different. This might be due to different phonon spectra, or to completely different mechanisms of energy supply and transfer. For example, we speculate that the energy necessary for ion motion in ionic crystals and in superionic conductors arises from ion-phonon coupling, leading to values of Δ_0 between 150 and 200 meV.

To clarify these points, further theoretical models are necessary. In particular, for systems with large densities of states and electron concentrations of 10^{18} cm^{-3} and larger, electron-electron interactions can result in the absorption and emission of Coulomb energy. In addition, further study of the values of Δ_0 in a wide range of circumstances may prove informative. Finally, the same ideas may be applied to such phenomena as variable range hopping. This will be discussed elsewhere.

Note added in proof. Peacock-Lopez and Suhl [Phys. Rev. B **26**, 3774 (1982)] have shown, in a very general way, that one obtains the compensation law by counting the ways in which the heat bath can furnish the energy required to surmount an activation barrier. This general approach permits them to show that Δ_0 or T_0 should be proportional to a characteristic energy of the heat bath, such as the Debye energy for phonons, or the exchange integral for magnons. It does not permit them to obtain the dependence upon coupling constant, or a value for α. For the case of desorption of adatoms from a solid surface, assuming coupling to longitudinal phonons, they perform a detailed calculation. From this they obtain an expression from which, in principle, complete expressions for Δ_0 and α may be obtained.

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[37] This was pointed out anonymously by one of the referees of YM.