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Dynamics of atomic diffusion in condensed matter: origin of the Meyer–Neldel compensation law

K. Shimakawa · M. Aniya

Abstract A new model that explains the Meyer–Neldel rule of atomic diffusion processes in condensed matter is presented. Phonon absorption and emission processes by diffusing atoms are separately taken into account in the atomic jumping processes whereas in the conventional classical model of diffusion the phonon emission process is not explicitly taken into account. Excitation and relaxation of the accepted phonon modes in the system may cause Meyer–Neldel rule in atomic diffusion processes. It is emphasized that the numbers of atoms in the activated states dominate the diffusion processes.

Keywords Ionic transport · Meyer–Neldel law · Diffusion kinetics · Multiphonon emission · Ionic crystal

Introduction

The Meyer–Neldel rule (MNR) or compensation law is now a very well known phenomenon in wide class of materials. When a phenomenon X is thermally activated, it is written as [1]:

$$
\begin{aligned}
X &= X_0 \exp\left(-\Delta E / kT\right) \\
&= X_{00} \exp(\Delta E / E_{MN}) \exp\left(-\Delta E / kT\right)
\end{aligned}
\tag{1}
$$

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where the pre-exponential factor X_0 itself depends exponentially on the activation energy ΔE. Here E_{MN} is called the Meyer–Neldel energy. The MNR is applied to both the physical and chemical kinetics (in some types of reaction) and to the thermodynamics (e.g. electron occupation related to Fermi–Dirac or Boltzmann statistics).

The expression given in Eq. (1) has a universal form for any thermally activated phenomenon. There is an argument that the MNR should have universal origin. Yelon et al. [1] emphasize that a multi-excitation process, for example multiphonon excitation, is the origin of the MNR: a large change in entropy associated with overcoming a potential should be involved in a thermal process. The idea is that this multi-excitation entropy (MEE) has a primary role in kinetics. The main point is that entropy should not be ignored in any reaction, or kinetic or thermodynamic process. Yelon et al. [1] and Emin [2] claim that the MNR should be found in materials in which small polarons with multiphonon processes dominate electron transport. Okamoto et al. [3] have discussed the universality of MNR on the basis of a specific mathematical background, i.e., the Laplace transform in the energy space E, and reached the same conclusion as that by Yelon et al. [1].

It is however, still not easy to find the physical background of MEE as a common physical basis for any material system. Therefore, we will discuss here a specific phenomenon for each material system. Electron transport in hydrogenated amorphous silicon (a-Si:H) [4] and amorphous chalcogenides (a-Chs) [5] are good examples for discussing the MNR. Whereas E_{MN} takes a value of approximately 40 meV for a-Si:H and 20–80 meV for a-Chs, $\sigma_{00} \approx 1$ S cm^{-1} reported for a-Si:H is very much larger than that for a-Chs. (10^{-5}–10^{-15} S cm^{-1}). A model of the statistical shift of the Fermi level, i.e., shift of the Fermi level with temperature, is most commonly known as

the origin of the MNR observed in electron transport in a-Si:H. With appropriate assumption of the density-of-states (DOS) in a forbidden gap, this model explains well the experimental results [4]. In a-Chs, however, the experimental results cannot be explained by the statistical shift of the Fermi level [5].

Let us briefly discuss the polaron hopping with multiphonon processes, which is usually described as a thermally assisted transition of a charge carrier between two localized electronic states. A hop is completed when a carrier absorbs phonon energy and dissipates it to surrounding atoms, in which detailed balance conditions should be established. In a generalized adiabatic polaron hopping model [2], the MNR results from the carrier-induced softening of vibrations, i.e., a reduction in the stiffness of the associated atomic vibrations at the activated inter-sites. Generally speaking, in hopping kinetics, the downward hops in energy are slowed by the need to emit multiple phonons. An example of this is the well-known "phonon bottleneck" in quantum dots, in which the excited state cannot relax to the ground state because of energy mismatch [1, 6].

Now, we focus on atomic transport, i.e., dynamics of atomic diffusion or ion transport. Although the MNR is mostly reported in disordered materials, it is also observed in the temperature-dependent diffusion coefficient in crystalline solids [1, 7]. In the following section, we will look for the origin of the MNR in atomic diffusion processes by discussing a new proposal of diffusion kinetics in solid states.

Atomic diffusion kinetics

Let us first discuss the most accepted and usual model of atomic diffusion. Figure 1 shows a schematic view for the local energy profile; (a), (b), and (c) represent the sites through which the moving atom passes and ΔU corresponds to the internal energy change which is accompanied by the atomic movement (jumping) between sites (a) and (c).

The free energy change ΔG is given by:

$$\Delta G = \Delta U - T\Delta S \tag{2}$$

where ΔS is the entropy change and T is the temperature. The jump frequency of a particle from site (a) to (b) is given as:

$$v = v_0 \exp\left(-\Delta G/kT\right) = v_0 \exp\left(\Delta S/k\right) \exp\left(-\Delta U/kT\right) \tag{3}$$

when $\Delta S/k$ is replaced by $\Delta U/E_{MN}$ for some reason, Eq. (3) shows the MNR for the jumping frequency. In the diffusion of interstitial atoms, $\Delta S/k$ is estimated to be not large [8]
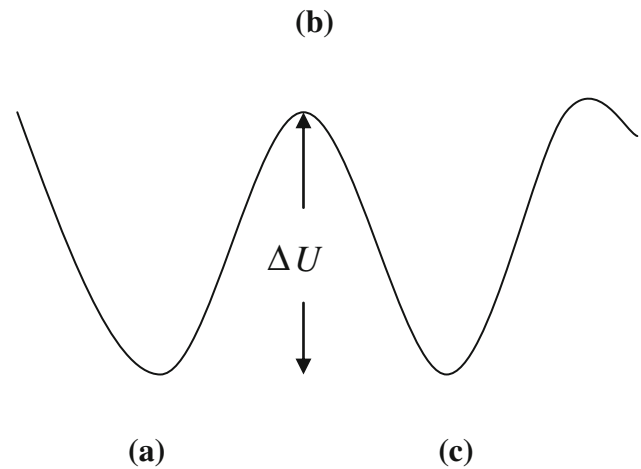

Fig. 1 Schematic view for the local energy profile. (a), (b), and (c) represent the sites through which the moving atom passes and ΔU corresponds to the internal energy change which is accompanied by the atomic movement (*jumping*) between the sites (a) and (c)

and hence this effect can be often ignored in the estimation of jumping rate. Yelon et al. [1] have emphasized that the entropy change should not be neglected when we discuss MNR in different phenomena. Their basic idea for the MNR is the multi-excitation of particles (electron or atom) which is closely dependent on entropy change.

Although the term $\Delta S/k$ can be important, we temporally treat the diffusion kinetics without this term. The configuration coordinate (CC) diagram shown in Fig. 2 may be useful for describing the energy change accompanied by atomic displacement.

The state (a) shown by solid curve represents the energy E vs. coordination q. The dashed curve shows the new configuration after atomic jumping to a neighboring site (state (c)). To complete this event, the jumping atom should cross the state (b) which is the crossing point between the states (a) and (c). The site (b) is called the activated state. To reach the activated state, a particle is required to obtain energy ΔU from the phonons of the media. ΔU can be given as [9, 10]:

$$\Delta U = \frac{q_0^2}{\sum_i \alpha_i^2} \tag{4}$$

where q_0 is the critical value in the coordinate q which is written as:

$$q = \sum_i \alpha_i Q_i = \sum_i \alpha_i \varepsilon_i^{1/2} \cos \omega_i t \tag{5}$$

Here, the displacement of an atom from the equilibrium lattice site q is given in terms of the superposition of lattice modes Q_i. ε_i is the energy of the mode Q_i, and α_i the weight factor of the mode that has frequency ω_i.
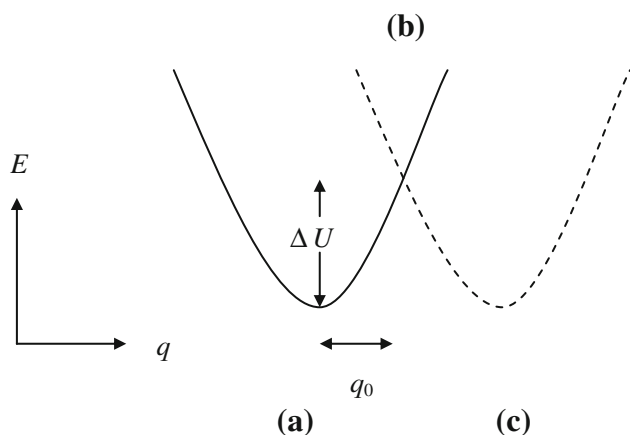
Fig. 2 The configurational coordinate diagram. The state (*a*), denoted by energy E vs. coordination q (*solid curve*), changes to a new configuration (*dashed curve*) after atomic jumping to a neighboring site (state (*c*)). Site (*b*) is called the activated state

Atomic movement from (a) to (b) is a thermally activated process and hence the rate of occurrence of such an event v_{ab} is given by:

$$v_{ab} = v_0 \exp(-\Delta U/kT) \tag{6}$$

where v_0 is the vibration frequency ($\sim 10^{13}$ s^{-1}). Note that state (b) is a transient state (activated state) and the transition to state (c) is still not complete. The process (b) to (c) corresponds to the energy release of the diffusing atoms; i.e. the kinetic energy of the diffused atoms obtained from the host is returned back through distortion and relaxation of the host. Thus the state (c) can be established by multiphonon emissions. The rate for this event v_{bc} can be described as:

$$v_{bc} = v_0 \exp(-c\Delta U/\delta) \equiv v_0 \exp(-\Delta U/E_{MN}) \tag{7}$$

by analogy with a quantum mechanical expression for the defect jump frequency at low temperature [11]. This equation is also analogous with the energy gap law used for description of the vibrational relaxation of a guest molecule in a solid or liquid [12, 13]. In Eq. (7), c is the coupling constant and δ is the energy of the accepting mode of vibrations which will be discussed in the next section, together with the experimental data.

Under thermal equilibrium conditions, the detailed balance between the ground state (a) and the activated state (b) should be established and hence:

$$N v_{ab} = n v_{bc} \tag{8}$$

where N is the number of atoms in state (a) (ground state) and n the number of atoms in state (b) (activated state). It is emphasized here that n corresponds to the actual number of diffusing atoms. Using Eqs. (6), (7), and (8), n is given as:

$$n = N \exp(\Delta U/E_{MN}) \exp(-\Delta U/kT) \tag{9}$$

It is noted that the ratio n/N is not simply given by the Boltzmann factor, although Eq. (9) is derived under thermal equilibrium.

The continuity law of flow should hold in the diffusion process as:

$$n D_{00} = ND \tag{10}$$

where D_{00} is the "diffusion coefficient in the activated state (b)" as will be discussed later, and D the actual diffusion coefficient which is experimentally observed. Using Eqs. (9) and (10), D is written as:

$$\begin{aligned} D &= D_{00} \exp(\Delta U/E_{MN}) \exp(-\Delta U/kT) \\ &\equiv D_0 \exp(-\Delta U/kT) \end{aligned} \tag{11}$$

We note that the MNR appears from the detailed balance condition of phonon absorption and emission processes, similar to the phonon bottleneck problem as stated in the previous section. In particular, the multiphonon emission rate to return to the ground state dominates the MNR in atomic diffusion processes. Yelon et al. [1] have also suggested the importance of the detailed balance condition in the electronic process, when the intermediate third state is involved in energy absorption and emission processes. The population of the intermediate state in this case depends on their kinetic behavior, i.e., depends on energy absorption or emission rate constants. This means that the thermodynamic behavior (population) is directly related to their kinetic behavior. The model of this paper, concerning ion or atom transport, is phenomenologically similar to this idea, i.e. the activated state in the atomic diffusion process corresponds to the intermediate state in the electronic process.

Examples of MNR in atomic diffusion

Because one of the most widely studied MNR cases is bulk diffusion in crystalline solids, examples of atomic diffusion are shown below. As examples, the diffusion of elements in crystalline Si, Ag, and KBr are considered. Open circles in Fig. 3 show experimental data for D_0 (Eq. 11) as a function of ΔU for many elements (metallic, semiconducting, etc.) in crystalline Si (data from Ref. [6]). The solid line shows a least-squares fit to the experimental data, which gives $D_{00} = 8 \times 10^{-7}$ cm^2 s^{-1} and $E_{MN} = 220$ meV, whereas D_0 at low energies is much more scattered. Analogously, experimental data for different elements in crystalline Ag [14] and KBr [7], and their least-squares fits are shown in Figs. 4 and 5, respectively. The evaluated values for Ag are obtained as $D_{00} = 1 \times 10^{-5}$ cm^2 s^{-1} and $E_{MN} = 170$ meV and for KBr they are found to be $D_{00} = 8 \times 10^{-6}$ cm^2 s^{-1} and $E_{MN} = 93$ meV.

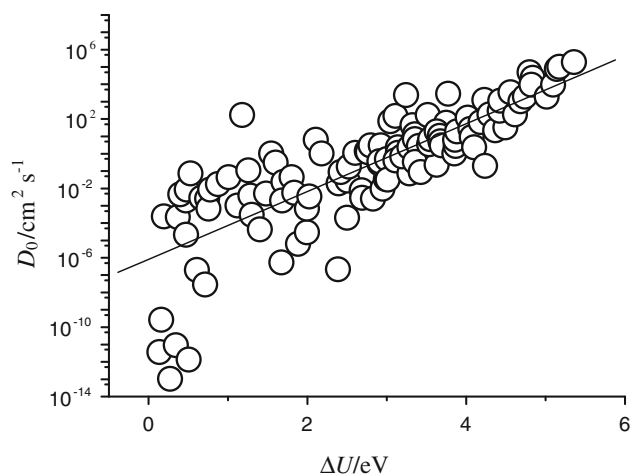Note that in the above experimental data, the diffusion of different elements in the same material is given. On the

Fig. 3 Experimental values (*open circles*) of D_0 for many different elements in crystalline Si (data from Ref. [6]) as a function of ΔU. The *solid line* shows a least-squares fit to the experimental data
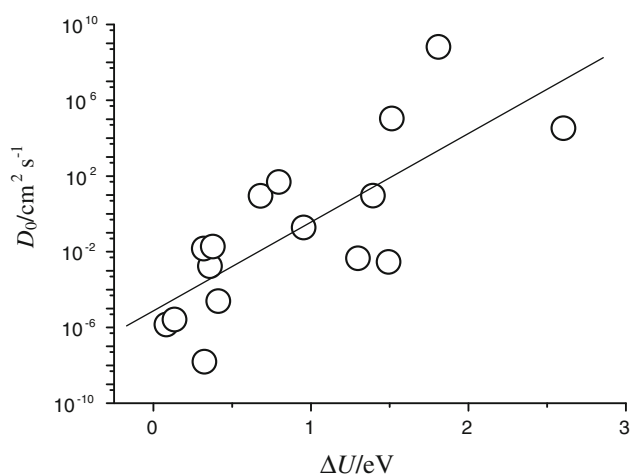

Fig. 5 Experimental values (*open circles*) of D_0 for different elements in KBr (data from Ref. [6]). The *solid line* shows a least-squares fit to the experimental data
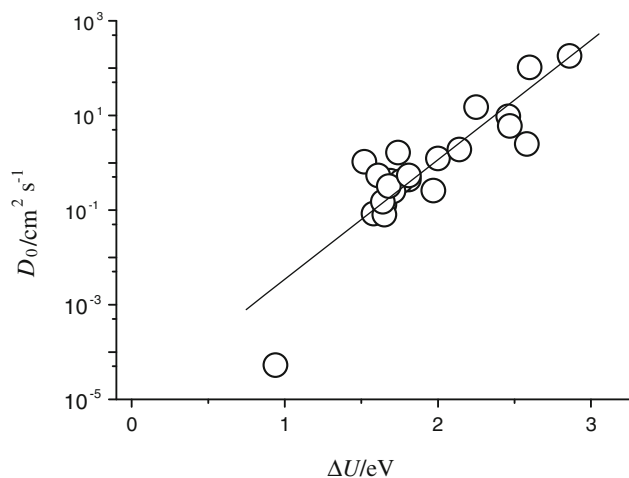

Fig. 4 Experimental values (*open circles*) of D_0 for different elements in crystalline Ag (data from Ref. [14]). The *solid line* shows a least-squares fit to the experimental data
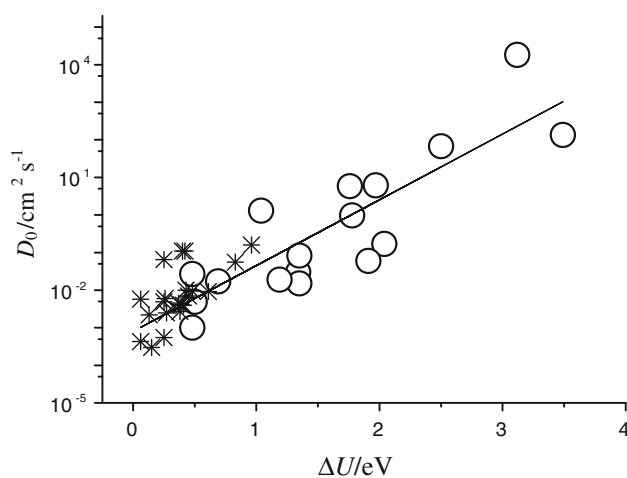

Fig. 6 Experimental values of D_0 for O (*open circles*) and H atoms (*stars*) in different metals (data from Ref. [14]). A least-squares fit to the experimental data is given by the *solid line*

other hand, Fig. 6 shows experimental values of D_0 for O and H atoms in different metals [14]. D_0 for both O and H seems to follow the same trend, although the values of D_0 for H are confined to lower ΔU only in comparison with those for O atoms. It is therefore concluded that there is no essential difference between the diffusion processes of O and H atoms. A least-squares fit to the experimental data given by a solid line gives $D_{00} = 8 \times 10^{-4}$ cm^2 s^{-1} and $E_{MN} = 250$ meV for both H and O.

From the above examples we obtain $D_{00} \sim 10^{-3}$–10^{-7} cm^2 s^{-1} and $E_{MN} \approx 100$–250 meV. The values of E_{MN} for atomic diffusion are reported to be in the range of 25–200 meV, typically between 150–200 meV [1]. Note that the values of E_{MN} for atomic diffusion are larger than

those reported in a-Si:H and a-Chs [1–3]. This clearly shows the difference between systems involving electron or atom transport.

We should discuss why large E_{MN} values compared with electronic systems are observed in atomic diffusion. The relaxation of the energy carried by the diffusing atom in the excited state is described by Eq. (7). Successful atomic migration occurs when the diffusing atom goes to state (c), as illustrated in Fig. 2. Such a successful migration is accompanied by the generation of a space necessary to accommodate the diffusing atom. In other words, it is accompanied by the generation of phonons whose atomic displacements favor accommodation of the diffusing atom. An example of such a phonon mode could be the zone

boundary phonons, where the opposite phase atomic displacement creates a space for the diffusing atoms [10]. This observation implies that there are specific channels for relaxation of excited state energy. For instance, for the case of relaxation of the CN^- stretching vibration in silver halides, it has been reported that the number of relaxed modes, N_{re}, is approximately 5 [13]. When the matrices are alkali metal halides, this quantity increases to the range 10–25. In these evaluations the value of $c = 1.9$ for the coupling constant is used. On the basis of these observations, an approximate estimate of E_{MN} (= δ/c) is given below.

As mentioned above, strong candidates involved in the accommodation of diffusing atoms are phonons near the zone boundary. The typical energies E_{ph} of these phonons are 10 meV for acoustic phonons and 25 meV for optical phonons. Because δ (in Eq. 7) can be given as the product $E_{ph} \times N_{re}$, E_{MN} is approximately estimated to be 150 meV, when we take the values of $E_{ph} = 20$ meV, $N_{re} = 15$, and $c = 2$.

Finally, we want to discuss the physical meaning of the prefactor D_{00} which appeared in Eq. (11). As already stated, D_{00} should be the diffusion coefficient in the activated state (b) illustrated in Fig. 2. Therefore, in the activated state, the diffusing atoms are regarded as freely moving atoms. Then, D_{00} can be given by:

$$D_{00} = \frac{1}{6} v_0 l^2 \tag{12}$$

where l is a length of the activated area, which should be less than the interatomic distance of the system. By assuming $v_0 = 10^{13}$ s^{-1} which should be close to E_{ph} and $l = 1 \times 10^{-8}$ cm, for example, D_{00} is estimated to be approximately 1.6×10^{-4} cm^2 s^{-1}, which is in the observed range of 10^{-3}–10^{-7} cm^2 s^{-1}. Note that the diffusion coefficient in the activated state may correspond to the so-called "microscopic" diffusion coefficient of band (free) electrons in electron transport [15].

Conclusions

A new model for atomic diffusion in solids has been proposed. The diffusing atoms are excited by absorbing energies from the various phonon modes of the hosted solid systems, and these atoms then relax by emitting specific phonons. This means that the dynamics of phonon absorption and emission are different. Under thermal equilibrium conditions, a detailed balance between the ground and activated states has been taken into consideration in the diffusion processes. The model proposed here thus predicts the MNR in atomic diffusion processes and the estimated physical results give reasonable support to the model.

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