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Investigation of the Meyer–Neldel compensation rule in binary selenium-based amorphous semiconductors

M.F. Kotkata [a,*], Sh.A. Mansour [b]

[a] Semiconductors Technology Lab, Faculty of Science, Ain Shams University, Cairo-11566, Egypt
[b] Basic Engineering Science Department, Faculty of Engineering, Menofia University, Shebin El-Kom, Egypt

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ABSTRACT

This paper contributes to a series of work analyzing the Meyer–Neldel compensation rule (MNCR) for various binary Se-based amorphous semiconductor systems. These systems are classified into two groups relying on the coordination number of the stoichiometric compound in each of the binary systems ($\langle r\rangle = 2.4$ and $2.4 \langle r\rangle \leq 2.67$). The estimated shift in the Fermi level of the investigated materials declares the physical basis of the MNCR behavior for DC conductivity where the activation energies (ΔE) are commonly measured around and above room-temperature. Also, the obtained MN energy (E_{MN}) values, supporting the electronic polaron hopping model resulted from the carrier-induced softening vibrations, provide a clearer physical picture for origin of the rule. In this consensus, one can realize the concept of multiple excitations entropy, that reserved for the large vibrations accompanied large ΔE, dominates the correlation between the two MNCR parameters (true pre-factor σ_{00} and E_{MN}) for all investigated systems in both groups.

1. Introduction

The Meyer–Neldel (MN) rule, known as the compensation law, was established empirically in 1937 [1] and subsequently examined by different authors for various thermally activated phenomena. The MN compensation rule (MNCR) states that the temperature-independent prefactor of Arrhenius diffusion constant increases exponentially with increasing the activation energy ΔE. This effect acts to compensate for the decrease in the temperature-dependent factor with increasing activation energy as:

$$D \propto \exp(\Delta E/kT_0)\exp(-\Delta E/kT) \tag{1}$$

where k is the Boltzmann constant, T and T_0 are the ambient and MN temperatures, respectively. Thus, the diffusion constant, $D \propto \exp(\Delta E/k)(1/T - 1/T_0)$, falls or rises with increasing ΔE depending on whether $T < T_0$ or $T > T_0$, [2]. In fact, the MN phenomenon is observed in variety of materials, and its ubiquity provides a compelling challenge to workers in condensed matter. It can occur in many situations involving an activated process. In the case of a thermally activated DC electrical conduction, the MNCR states that the conductivity (σ) obeys an Arrhenius equation similar to that illustrated in (Eq. (1)); i.e.,

$$\sigma = \sigma_0 \exp(-\Delta E/kT). \tag{2}$$

The thermal activation energy of conduction ΔE correlates with the apparent pre-factor σ_0 as:

$$\sigma_0 = \sigma_{00}\exp(\Delta E/E_{MN}) \tag{3}$$

where σ_{00} and $E_{MN}(kT_0)$ are constants obtained by averaging over a group of related materials. σ_{00} is often called the MN pre-exponential factor, and E_{MN} as the MN characteristic energy. Eq. (3) is referred to as the MNCR. The validity of MNCR is investigated extensively for amorphous semiconductors by different research groups. Each group is concerned in studying related samples that have one common transport mechanism. Several models have been proposed to describe this rule irrespective of some issues that are still under debate, [cf. [3] and references cited therein]. Fang [4] proposed a model for MNCR in activated processes of annealing. Robert [5] and Cohen et al. [6] proposed that the MNCR in amorphous or polycrystalline semiconductors may originate from exponential tailing of the majority band states. For organic semiconductors, Kameny and Rosenber [7] proposed a model where the electron tunnel passes through intermolecular barrier from activated energy states of the organic molecules. Shimakawa and Abdel-Wahab [8] indicated that similar situation, phenomenologically, may occur in chalcogenide glasses. Yelon et al. [9] used the multi-excitations entropy (MEE) model as an explanation of MNCR using the data of [10] analyzed by [8]. Nevertheless, the common limitation for most of the above models was that they could not provide a universal explanation of the MNCR in all materials for a particular thermally activated process or vice versa.

In a recent review [11], the MNCR has been examined for mixed isoelectronic chalcogens systems in which the addition of S and/or Te to Se

* Corresponding author.
E-mail addresses: mfk.asu@gmail.com (M.F. Kotkata), shehab_mansour@yahoo.com (S.A. Mansour).

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leads to a formation of 1D material. This paper aims at presenting the evidence of MNCR for various amorphous binary selenium-based chalcogenide systems of the general formula Se–X, where X is a guest element from different groups of the periodic table (Cu, Ga, In, Tl, Ge, P, As, Sb and Bi). Addition of any of these elements to Se forming Se–X leads to 2D–3D structural units.

2. Coordination numbers of Se–X

The structural units of a system, as a rule, that constitute the glass network, are determined by the nature and composition of the compounds existing in that system. In a covalently constructed structural unit of chalcogenide glass, the maximum number of neighbors of an atom is equal to that of valance bonds that the atom can form, [10]. On the other hand, the structural defects are very important for the chemical stability of a glass. In this respect, glasses can be characterized as being composed of normal structural bonds as well as deviant electronic configurations, and the activity of both cannot be separated from their surrounding environment [12].

Selenium belongs to group VI of the periodic table and is characterized by an outer electronic shell of six electrons $s^2p_x^2p_y^1p_z^1$. Only the two odd electrons are involved in the formation of strong covalent bonds to build the inorganic polymeric network. It is commonly assumed that the *s* electrons lie well below the *p* states and do not contribute to the bonding [13,14]. Indeed, each Se atom can be viewed as generating a tetrahedron formed by the repulsion of two bonding electrons pairs and two nonbonding lone-pair electrons. As a result, the main structural building unit responsible for the formation of the solid is an infinite chain as represented in Fig. 1, where the structure and bond lengths are schematized, [15]. The nature of the bonding, responsible for the interchain cohesion, is of Van der Walls origin and results from dipole/dipole interactions.

It is obvious that a chain-like framework will result in a poor rigidity with a low glass transition temperature (T_g). As an example, the Se glass, itself, suffers from a low value of T_g (<50 °C, [16]) incompatible with practical applications. Consequently, the development of glass compositions having network dimensionality between 1D, 2D or 3D is considered significant to ensure values of T_g superior to the arbitrary average value of 130 °C. In order to maintain the covalent character of the network while increasing the dimensionality, Philips [17] and Thorpe [18] have developed a general theory predicting the network rigidity of chalcogenide glasses based on the average coordination number $\langle r\rangle$ defined as the average number of covalent bond per atoms. Based on topological constraints of counting methods, Phillips [17] proposed that the network is optimally connected at $\langle r\rangle = 2.4$, where the number of degrees of freedom just exhausts the number of constraints imposed by bond-bending and bond-stretching forces. Thorpe [19] expanded this argument suggesting that, below $\langle r\rangle = 2.4$ the glass network is composed of floppy or zero-frequency vibrational modes and is unbraced or under-constrained. The converse is true above 2.4, where the glass is over-braced or over-constrained. When $\langle r\rangle$ reaches 2.4, the number of zero-frequency modes should diminish to zero and rigidity should percolate. Later, Tanaka [20] showed that there exists, yet, another structural phase transition at $\langle r\rangle = 2.67$; glasses with $\langle r\rangle \le 2.67$ may have low-dimensional structures; whereas, when $\langle r\rangle > 2.67$ glasses are cross-linked three dimensionally (3D). Thus, there are two kinds of topological thresholds observed in chalcogenide glasses when their properties are studied as a function of $\langle r\rangle$: one is at $\langle r\rangle = 2.4$, the "rigidity percolation" threshold, and the other is at $\langle r\rangle = 2.67$, the "2D → 3D" threshold.

The concept of $\langle r\rangle$ is considered in the present work to categorize the investigated binary Se-based chalcogenide systems. Such classification depends on both the glass forming ability and the rigidity of the stoichiometric compound (or compounds) of each system. In this consensus, it is worth highlighting that the considered value of $\langle r\rangle$ corresponds to the stoichiometric compound of each system. The first group (GA) is that where $\langle r\rangle = 2.4$. The Se–Bi system is an example of such group. It shows a deviation from the stochastic agglomeration theory prediction at an average of $\langle r\rangle = 2.4$, [21]. This theory provides a quantitative means to analyze the compositional trends in terms of T_g. The second group (GB) is for systems with $2.4 < \langle r\rangle \le 2.67$ referring to networks that are too rigid and resulted in poor glass forming ability, [20]. The Se–Ge system is an example for GB, where the value of $\langle r\rangle = 2.67$ coincides with the stoichiometric compound $GeSe_2$ that confirms

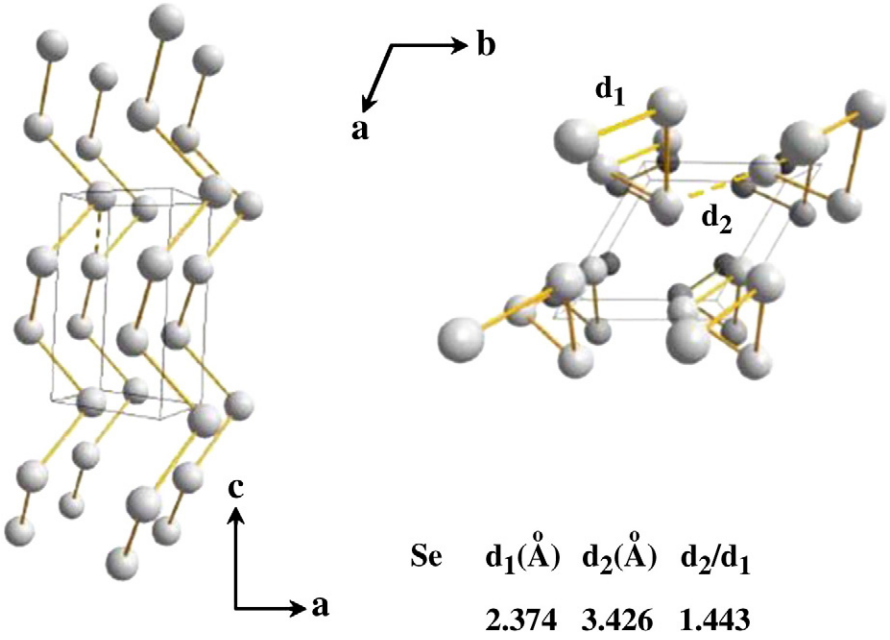

Fig. 1. Hexagonal selenium with its relevant bond lengths, [15].