COMPENSATION EFFECT IN KINETICS OF CRYSTALLIZATION IN DISORDERED MATERIALS[♣]

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The paper presents the basic idea of the possible explanation of the compensation effect in crystallization processes in amorphous materials. The starting point of our consideration is the assumption that the crystallization processes and catalyzis are closely associated with diffusion. We suppose compensation effect for above mentioned phenomena to be the result of the compensation effect (or Meyer-Neldel rule) in diffusion. An understanding of the kinetics of crystallization in glasses is very important for practical application of disordered semiconductors. Many modern electronic solid-state devices such as electrophotographic photoreceptors employed in today's photocopiers, solar cells, organic field-effect transistors (OFETs), and organic light-emitting diodes (OLEDs) are generally based upon noncrystalline materials. Chalcogenide glasses are important group of these materials. They have become attractive materials, which form the basis for phase-change optical recording (CD and DVD) and electronic phasechange memory (PCM) technologies. The aim of research in this area is to increase the reliability of recording information, as well as increased density recording. Differential scanning calorimetry (DSC) is valuable for the quantitative experimental study of crystallization processes in different glassy systems. Diffusion processes - as we believe – have a considerable impact on the phenomena of chemical catalyzis. The paper shows the possible explanation of the validity of the compensation effect in the heterogenous catalytic phenomena using the simplified model.

1. Introduction

The study of amorphous to crystalline phase change is important for the development of new disordered semiconductors (chalcogenide glasses) as better phase change recording materials [1-3]. Various quantitative methods have been suggested to evaluate the level of stability of the glasses. Some of these methods are based on the characteristic temperatures such as the glass transition temperature (T_G), the on-set crystallization temperature (T_0), the peak crystallization temperature (T_C) and the melting temperature (T_M) [4 -7]. More criterions are based on reaction rate constant of crystallization. The determination of rate constant is a subject of great interest from application as well as scientific point of view [4-7]. An understanding of the kinetics of crystallization in glasses is important for the manufacturing of glass-ceramics and in preventing devitrification, too.

1.1 Kinetics of crystallization

Crystallization rates are sometimes measured directly in the microscope [8-11] but this method could not be applied to glasses in which nucleation and crystallization occurred in times below 1h [7]. Differential scanning calorimetry (DSC) is valuable for the quantitative study of crystallization in different glassy systems [11-13]. The crystallization phenomenon in chalcogenide glasses can be experimentally investigated using isothermal and non-isothermal methods. In isothermal method, the sample is brought near to crystallization temperature very quickly and then any physical quantity which changes drastically is measured as a function of time. In non-isothermal method, the sample is heated at a fixed rate and the physical parameter is recorded as a function of temperature. Any physical parameter, which changes drastically, can be taken as a measure of extent of crystallization as a function of time. A disadvantage of the isothermal method is the impossibility to reach a test temperature instantaneously and during the time in which the system needs to stabilize, no measurements are possible. However, non-isothermal methods based on constant heating rate experiment do not have this drawback.

1.2 Isothermal transformation

During the isothermal transformation, the extent of crystallization α of a certain material is represented by the Avrami's equation [14-16]

$$\alpha(t) = 1 - \exp(-(Kt)^n) \tag{1}$$

where K is rate constant and n is the order parameter which depends upon the mechanism of crystal growth. In general, crystallization rate constant K increases exponentially with temperature indicating that the crystallization is a thermally activated process. Mathematically, it can be expressed as

$$K = K_o \exp\left(-\frac{W_c}{kT}\right) \tag{2}$$

Here W_c is the activation energy of crystallization, K_0 the pre-exponential factor and k the universal Boltzmann constant. In Eq. 2 W_c and K_0 are assumed to be practically independent of the temperature (at least in the temperature interval accessible in the calorimetric measurements).

The *a-c* phase transformation in chalcogenide glasses is accompanied by a continuous change of the electrical conductivity σ, which is a sensitive structural parameter. The extent of crystallization α can be calculated using the following relation [17]:

$$\alpha = \left(\frac{\ln\sigma - \ln\sigma_a}{\ln\sigma_c - \ln\sigma_a}\right) \tag{3}$$

The values of σ_a and σ_c were calculated by plotting the time dependence of lnσ during the *a-c* phase transformation for each glassy alloy at different annealing temperatures. Once the values of α as a function of time are known at different isothermal annealing temperatures, the kinetic parameters (K_o and W_c) can be calculated using Eqs. 1-3.

1.3 Non-isothermal crystallization

In non-isothermal crystallization, it is assumed that there is a constant heating rate in the experiment. The relation between the sample temperature T and the heating rate β can be written in the form:

$$T = T_1 + \beta t, \tag{4}$$

where T_1 is the initial temperature.

The values of activation energy of crystallization W_c and the pre-exponential factor K_0 in Eq. 2 can be (in case of the non-isothermal crystallization method) evaluated by the equation

$$\ln\left(\frac{\beta}{T_c}\right) = \left(-\frac{W_c}{RT_c}\right) + \ln K_o \tag{5}$$

using the plots of $\ln(\beta/T_c)$ against $1/T_c$ [3]. In Eq. 5, W_c and K_o are assumed to be practically independent of temperature, too. The Eq. 5 was derived by Augis and Bennett in [18] from the classical Johnson-Mehl-Avrami (JMA) theoretical model [14-16]. This method has an extra advantage that the intercept of $\ln \beta/T_C$ vs. $1/T_c$ gives the value of pre exponential factor K_0 of Arrhenius equation. The experimental results show that W_c values obtained by Eq. 5 are in good agreement with the W_c values obtained by well known Kissinger's relation [19] and relation of Matusita and Sakka [20]. Eq. 5 has been used by various scientists [4, 21-24].

1.4 Meyer-Neldel rule

The MN empirical rule was discovered by Meyer and Neldel in 1937 by investigation of electrical conductivity of some semiconducting substances [25]. Most semiconductors exhibit an exponential temperature dependence of the conductivity, $\sigma(T)$

$$\sigma = \sigma_0 \exp(-\frac{W}{kT}), \tag{6}$$

where σ_o is a constant and W – activation energy [26-28]. For many classes of materials, especially chalcogenide glasses, amorphous silicon, organic semi-insulators,… experimental evidence suggest that a correlation exists between the activation energies and pre-exponential factors in the following form [3, 29]

$$\ln \sigma_0 = bW + \ln \sigma_{00}, \tag{7}$$

where b and σ_{oo} are constant. This relation can be written as

$$\sigma_0 = \sigma_{00} \exp(\frac{W}{kT_0}), \tag{8}$$

here $b = 1/kT_o$. The Eq. 8 gives the dependence of pre-factor σ_o on the activation energy W and represents Meyer-Neldel empirical rule, or the compensation rule which was discovered by Wilson [30] in 1908. Constant σ_{oo} is often called the Meyer-Nedel pre-exponential factor and kT_o the MN characteristic energy. The MNR is generally observed in disordered materials. In the class of amorphous semiconductors, the MNR has been reported for a-Si:H films in which W is varied by doping by surface absorption, light soaking or by preparing films under different conditions. This rule has also been observed for liquid semiconductors and fullerenes. The validity of MNR has been reported in the chalcogenide glasses. However, in case of these glasses this rule is observed by the variation of activation energy W on changing the composition of the glassy alloys in a specific glassy system [3].

Evidence of MN rule [2,3] has been accounted for a number of activated phenomena such as solid state diffusion in crystals and polymers, dielectric relaxation and conduction in polymers, thermally stimulated processes in polymers and electric conduction in amorphous semiconductors, less effort has been done to observe MN rule in kinetic phenomena such as crystallization phenomenon.
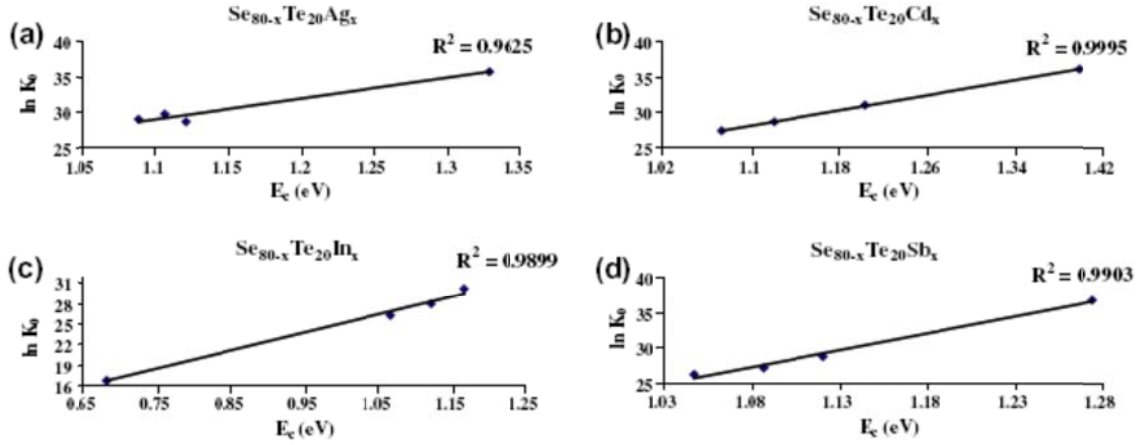
Fig. 1. Observation of MNR in Se$_{80-x}$Te$_{20}$M$_x$ alloys (M = Ag, Cd, In, Sb)
for thermally activated non-isothermal crystallization [3, 4].

1.5 MNR in crystallization processes

The Meyer-Neldel rule in crystallization describes following exponential relation between the activation energy W and the preexponential factor K_o, which appears in the Eq. 2:

$$K_o = K_{oo} \exp\left(\frac{W_c}{kT_o}\right) \qquad (9)$$

Here K_{00} and T_0 are positive constants [3].

The applicability of MNR for thermally activated isothermal crystallization in chalcogenide glasses of the Se–Ge–Sb system was firstly reported by Bordas et al. [31,32]. By annealing some Se–Ge–Sb glasses, they observed two crystalline phases: Sb$_2$Se$_3$ and GeSe$_2$. According to Bordas et al. such a compensation effect may be attributed to the primary crystallization of Sb$_2$Se$_3$ phase.

In the [3, 4] it is reported the applicability of Meyer-Neldel rule for pre-exponential factor of non-isothermal crystallization in Se$_{80-x}$Te$_{20}$M$_x$ alloys (M = Ag, Cd, In, Sb) using DSC technique. The authors have observed strong correlation between pre-exponential factor K_0 and activation energy $W_c(= E_c)$. The result (Fig. 1) shows that the activation energy and pre-exponential factor satisfies the Meyer and Neldel rule in form

$$\ln K_o = \ln K_{oo} + \frac{W_c}{kT_o} . \qquad (10)$$

2. Explanation of the Meyer-Neldel rule

Many attempts have been made to explain the MNR (compensation effect) for various processes. Up to now there is not the generally accepted theory explaining the MN rule satisfyingly [3].

2.1 MNR and electrical conductivity of semiconductors

Basic ideas concerning the MNR explanation in the case of electric conductivity in non-crystalline semiconductors, namely, in chalcogenide glasses, non-crystalline silicon, Si and Si:H were presented in the works [33-36]. Validity of the Meyer-Neldel rule in non-crystalline semiconductors

can be explained assuming that recombination transition of an electron from conduction band to valence band is conditioned by emission of number of monoenergetic phonons whose total energy corresponds to the width of forbidden band (and so to the energy extracted in transition). Probability of such complex process is determined by number of emitted phonons. This probability exponentially decreases with increasing number of phonons and consequently with the width of the forbidden band. The probability of recombination influences equilibrium concentration of free electrons in conduction band and subsequently electric conductivity. In such a way we have finally obtained the relation which is equivalent to the Meyer-Neldel rule [33-36].

2.2 MNR in crystallization processes

Crystallization process is closely related to diffusion of matter particles. Validity of the MNR in crystallization processes is - as we believe – the result of the validity of MNR in diffusion of particles. In our article we postulate that the crystallization rate K is directly proportional to the diffusion coefficient D, so K ~ D, respectively

$$K = fD, \tag{11}$$

where f is a constant. If we prove that the diffusion coefficient D in this case meets MNR rule, we can also confirm the MNR rule for crystallization rate in this case. From the relation

$$D = D_{00} \, \exp(\frac{W}{kT_0}) \exp(-\frac{W}{kT}) \tag{12}$$

and Eq. 11 follows

$$K = K_{00} \, \exp(\frac{W}{kT_0}) \exp(-\frac{W}{kT}) \tag{13}$$

Concerning the correlation between pre-exponential factor K_o and activation energy W comparing Eq. 1 and Eq. 2 we get

$$K_o = K_{00} \, \exp(\frac{W}{kT_0}) \tag{14}$$

It is this relationship that describes the experimentally found dependence MNR presented in Fig. 1 in logarithmic form. In the following we will focus on an explanation of the MNR in diffusion.

2.3 MNR in diffusion processes

Diffusion is a process proceeding on microscopic level and possessing a broad variety of forms. Diffusion plays important role in solids [4, 26-28]. Numerous micro-structural changes and numerous chemical reactions in solid state take place through solid state diffusion, i.e. the movement and transport of atoms in solid phase [4, 26-28]. Diffusion also takes place along line and surface defects which include grain boundaries, dislocations, inner and outer surface, etc. Observations show that the diffusion often has excitation (activation) character. This is expressed by activation dependence of diffusion coefficient D on temperature T in a form

$$D = D_0 \, \exp(-\frac{W}{kT}), \tag{15}$$

where W is the activation energy of diffusion process and D_o je pre-exponential factor. This relation resembles to the Eq. 8 for electrical conductivity. In case of diffusion in corresponding

formula instead of electrical conductivity of semiconductor emerges the diffusion coefficient D. If the MNR is valid then for diffusion pre-exponential factor D_o holds

$$D_0 = D_{00} \exp(\frac{W}{kT_0}),$$ (16)

where D_{oo} and T_o are constants. The Eq. 1 is analogy of the Eq. 8. For diffusion coefficient of upper mentioned group of substances holds

$$D = D_{00} \exp(\frac{W}{kT_0}) \exp(-\frac{W}{kT})$$ (17)

2.3.1 Band model for impurity diffusion

Our further aim will be to explain the physical nature of MNR (Eq. 16) for diffusion processes. We will start our reasoning by so called band model of diffusion. The suitable band model for description of activation processes appears that one, that is successfully used for description of electric properties of semiconductors. One typical feature of that model is the existence of forbidden energy gap separating the valence band from the conduction band. The band model prepared the way for explanation of the MNR by electrical conductivity of non-crystalline semiconductors [33-39]. Analogical band approach, likely, is suitable for description of diffusion processes in solids and liquids. The fundamentals of this model will be described later. The band model of particle diffusion – e.g. impurity atoms in a non-crystalline substance, assumes that impurity atoms of diffusing matter are to be found at low energies in the ground (basic) band therefore in the band of low (nearly zero) mobility. In this simplified model we shall consider mobility of these particles in the ground (basic) band to be zero. By sufficient energy the particles (atoms) of the ground band can be exited over the forbidden band into the band of non-zero mobility. The atoms need sufficiently enough of energy to this transition. This process is called activation one. The concentration n of impurity atoms in the band of non-zero mobility will be determined by the relation

$$n = n_o \exp(-W/kT).$$ (18)

This concentration is closely connected with the coefficient of diffusion $D \approx n$, so that

$$D = D_o \exp(-W/kT).$$ (19)

Experiments with diffusion showed that quantities n_o a D_o at the changes of activation energy W very often change in according to empirical Meyer-Neldel rule, namely as

$$n_o = n_{oo} \exp(W/kT_o),$$

resp.

$$D_o = D_{oo} \exp(W/kT_o),$$ (20)

where n_{00}, D_{00} and T_0 are constants. Furher will be shown that MNR dependence (Eq. 18) can be explained under specific conditions connected with transition of excited atoms from the diffusion band (from a state of non-zero mobility) to the ground – non-active band (of zero mobility).

2.3.2 Dependence of diffusivity D on activation energy W

Our model assumes that there are not energy levels of significant concentration in forbidden band.

Conditions of the MNR validity in a given diffusion process are connected with transition of an atom from the diffusion band into the ground band. A transition of an atom from diffusion band to basic band in disordered materials proceeds predominantly by production of phonons. The total energy of produced phonons will correspond to that one released in atom transition. It appears on the level of

energy corresponding to the forbidden band width equal to $2W$. Further, we shall assume that in a substance under consideration dominates phonon production which average energy is ΔE. It means, that phonon production of other phonons is negligible. At the transition of an atom from diffusion band to basic band gained energy $2W$ is used for production of N phonons each of them with energy ΔE so that $2W = N\Delta E$ or

$$N = 2W/\Delta E. \tag{21}$$

Let w_1 be the probability of production of one phonon which energy is equal to ΔE. Probability w_N of production of N phonons of equal energy due to the excited atom – lattice interaction will be

$$w_N = (w_1)^N. \tag{22}$$

If we write down probability w_1 as $w_1 = \exp(-\varepsilon_1)$ where ε_1 is a positive value, then probability w_N can be written with respect to Eq. 21 and Eq. 22 as

$$w_N = \exp(-N\varepsilon_1) = \exp(-\varepsilon_1 2W/\Delta E) = \exp(-bW), \tag{23}$$

where the constant b is given by

$$b = 2\,\varepsilon_1/\Delta E. \tag{24}$$

Eq. 23 gives at the same time the transition probability of an atom from diffusion to basic band. That one is proportional to the probability of production N phonons and thus proportional to the $\exp(-bW)$. With an increase of activation energy W, the probability of the transition of atom in to basic band according to Eq. 23 exponentially decreases.

2.3.3 Equilibrium concentration of excited particles and diffusivity coefficient

An equilibrium concentration n of excited atoms occurring in the diffusion band is a result of two opposite processes: one is the process of generation and the other one is the process of „annihilation of free atoms" in diffusion band. In equilibrium (or steady) state it holds $(dn/dt)_{gen} = (dn/dt)_{recom}$.
We shall assume, that the number n of excited particles generated in unit time is given as

$$(dn/dt)_{gen} = G = C_1\exp(-W/kT), \tag{25}$$

where C_1 is a constant. For an „annihilation" process we suppose that the relation

$$(dn/dt)_{recom} = R = n.C_2\exp(-bW) \tag{26}$$

is valid. Here C_2 is a constant. The number of annihilation in a unit of time is proportional to the number n. In equilibrium state $R = G$ is valid, so that $C_1\exp(-W/kT) = n\,C_2\exp(-bW)$
From that relation follows for equilibrium concentration n of free atoms

$$n = C_{oo}\exp(bW)\exp(-W/kT), \tag{27}$$

where C_{oo} is determined by the constants C_1 and C_2. It is known that diffusivity coefficient D is proportional to n: $D \approx n$. If mobility of free particles in diffusion band is independent on activation energy W (or that dependence is negligible) one can write with respect to Eq. 27

$$D = D_{oo}\exp(bW)\exp(-W/kT). \tag{28}$$

If we put $b = 1/kT_o$, the Eq. 28 takes the form identical with Eq. 15. At the same time it is valid

$$D_o \approx D_{oo} \exp(W/kT_o),\qquad\qquad(29)$$

that expresses the Meyer-Neldel rule (Eq. 14) for diffusion.

3. Discussion. Physical foundation of the diffusion band model

The best arguments in favor of presented hypothesis concerning band model of diffusion can one seek in physics of semiconductors. Just there has been for the first time elaborated and theoretical well-founded band theory of electrical conductivity of semiconductors. It resulted from the solution of the problem of an electron motion in periodic (electric) field of a crystal. If one replaces electron by other particle – say, by diffusing impurity atom – then analogical situation arises. Diffusing atom is also moving in a periodic force field of an atomic lattice. Moving atom is a particle which motion complies with laws of quantum mechanics. The difference is that; the atom has greater mass then electron. It does not change the essence of our analogy. In the case of diffusion it is inappropriate to speak about recombination, which is used by semiconductors. That is not significant for creation of a band structure. The band model of diffusion well fits activation character of diffusion and also the MNR for diffusion, as it was shown in preceding section. Moreover, the band model of diffusion enables to understand activation character and validity of the MNR at catalysis and other chemical processes and at phase transitions, too. The Meyer-Neldel rule can not be connected with each kind of diffusion in solid. Sometimes, the Arrhenius relation with constant pre-exponential factor can be valid. The MNR will be valid in case of such diffusion at which the transition from diffuse band into ground band over forbidden band is realized with emission of a number of phonons with relative low energies (compared to the width of energy gap). Transfer of particles in a substance proceeds mainly in diffusion band.

Next information about chalcogenide glasses and Meyer-Neldel rule in disordered semiconductors can be found in [40-44].
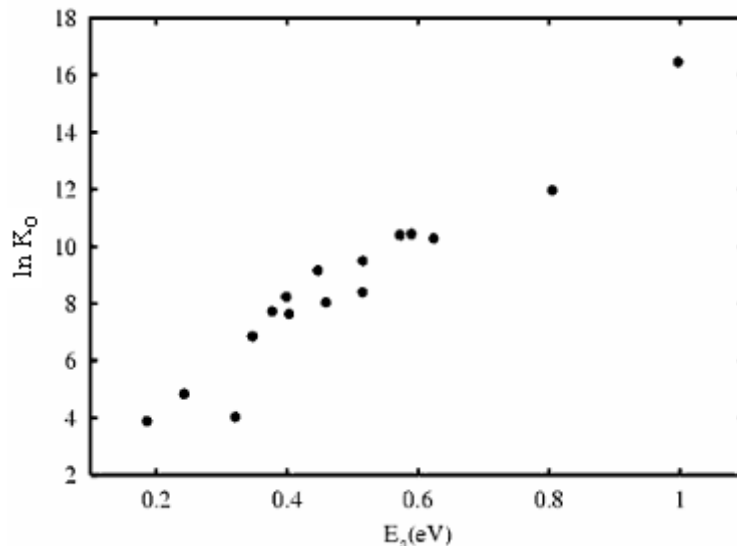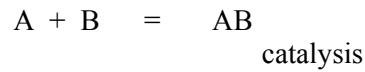

Fig. 2. Experimentally measured apparent activation energies E_a (= W) and catalyzis MNR prefactors K_o for ammonia synthesis over a number of bimetallic alloys ([45, 46]).

3.1 Surface diffusion, MNR and heterogeneous catalysis

Surface diffusion is a critically important concept in heterogeneous catalysis, as reaction rates are often dictated by the ability of reactants to "find" each other at catalyst surface. With increased temperature adsorbed molecules, molecular fragments, atoms, and clusters tend to have much greater mobility. Activation mechanism and MNR (Fig. 2) - as it is known - takes place also in catalytic processes [45, 46]. It seems to us, that diffusion is responsible for it.

Next, as an illustration we shall introduce a simplifying model of one sort of catalysis. Le us assume, that at catalytic synthesis of atoms of a type A with atoms of a type B; it means at catalytic reaction

$$A + B = AB$$
$$catalysis$$

it is in progress as follows:

Atom A is caught at the surface of metallic (catalyst) catalyzer (e.g. platinum) at the fixed position. Atom B is also caught at the surface of metallic catalyzer but it will be able to diffuse at the surface of the catalyzer. In fact, it will proceed - according to concept of band model, described above – in such a way that atom B will be in a state of zero mobility or in an excited state of non-zero mobility. Its activation energy will be W_B and it will participate in surface diffusion. Excited atom B can submit its energy through multiple creation of phonons with comparatively low energy in comparison to energy W_B. That process creates suitable conditions in which the MNR is valid, not only for surface diffusion of a particular atom B at the surface of catalyzer, but also for all long chain of such actions – catalytic process.

The catalytic chemical reaction – as it is believed – will be realized when diffusing atom B comes close enough to the fixed atom A. When catalytic reaction – in which participates the catalyzer, too – will be over, resulting molecule AB will be free. It is the product of catalysis. The number of AB will be proportional to the number of atoms B in the excited state, because only these atoms can participate in catalytic fusion with atoms A.

Just, above described process of catalysis will be conditioned by surface diffusion at least one type of atoms. Catalysis will show activation character, because such character has one link of a chain of actions. The MNR will be valid for catalysis, too. Analogical activation process can be connected with diffusion of A at the surface of a catalyst. If the activation energy W_A is much greater then the activation energy W_B only the process of one type will predominate.

3.2 The MNR at phase transitions

Diffusion plays an important role at phase transitions, too [3, 4]. It can represent one intermediate (interface) in a process of phase transformation. Diffusion can significantly contribute to the particle transfer between phases. If it is true, then an activation process affecting diffusion is at the same time an activation process of whole phase transition. It results to the validity MNR at phase transition.

3.3 Self-diffusion on Pd(111) from point of view of band model of diffusion

In this section we present the new view on the results of experimental investigation of the self - diffusion on Pt(111), that was published in [47]. Measurements, realised on the base of scanning tunneling microscopy show, that for given diffusion process the Meyer–Neldel compensation law is fulfilled. The activation energy (height of the barriers) for diffusion was found to be 350 meV. But an exceptionally high prefactor of 6×10^{16} s^{-1} was observed, which cannot be understood from point of view of standard theory of diffusion, e.g. in terms of vibrations of atom alone. This is the highest value of the pre-exponential factor observed so far for self-diffusion on Pt(111) metal surface. Hence, this pre-factor can not be identified with the vibration frequency of atom in the adsorption site.

The authors [47] were surprised by the high value of pre-exponential factor. They stated: „The high value of the prefactor $D_o = 5 \times 10^{16}$ s^{-1} (about four orders of magnitude greater than the commonly assumed value of $\approx 10^{13}$ s^{-1}) is, at least at first sight, quite puzzling". This value of pre-factor cannot be – according to above mentioned authors - understood from point of view of standard theory of diffusion, it means in terms of vibrations of the atom alone. Hence, this pre-factor can not be identified with the vibration frequency of the atom in the adsorption site.
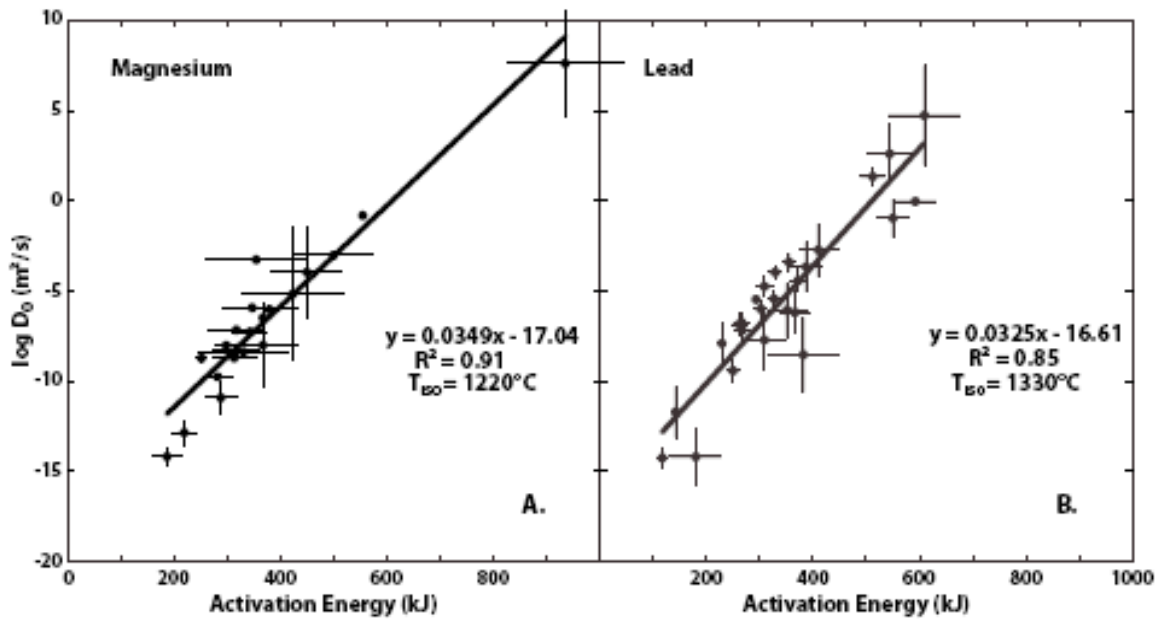
Fig. 3. Compensation diagrams for the diffusion of Mg (A.) and Pb (B.)
in all minerals in the database [48].

To support the band model of diffusion let us note that in terms of this model there is no dilemma. Diffusion process is according to the band model of diffusion not limited by vibration frequency and the movement of excited diffusing atom, governed by the laws of quantum mechanics, is not bound by the gradual transition of the atom through series of interstitial states. Diffusing atom may theoretically move in the excited state, which corresponds to a non-zero mobility (in terms of wave-mechanical) in one excitation transition even to a relatively greater distance. This distance is not affected by the value of the vibration frequency, which according to the standard vibration model usually is $10^{13}s^{-1}$. From the point of view of the band model of diffusion, great value pre-exponential factor is not at all problematic.

3.4 Diffusion in minerals

The interest of geologists for the diffusion processes and the MNR in minerals is understandable. Not surprisingly there is a significant effort to summarize the amount of obtained experimental results [48]. To illustrate this we give Fig. 3, where we see two graphs confirming the validity of MNR in these materials.

Although geologists have been thinking and writing about diffusion in minerals, magmas, and rocks since early in the 20th century, very few experimental measurements of diffusion in minerals by geologists were published until the 1960's [48]. The development of commercial electron microprobes in the late 1960's made it possible to measure compositional zoning in minerals on a micron scale, which provided both the motivation for and means for determining diffusion coefficients. Other technological advances (e.g., secondary ion mass spectrometry) have increased interest in diffusion data further, leading to a continual growth of published diffusion coefficients and to the application of a host of experimental designs and measurement techniques (e.g., vapor deposition, Rutherford backscattering, nuclear reactions) that have expanded the range of measurable diffusivities.

4. Conclusion

The paper presents an explanation of the validity of the Meyer-Neldel rule in the processes of

crystallization in the semiconducting glasses. We consider the validity of this rule for crystallization and catalyzis to be the result of the MNR validity in diffusion. Our consideration is based on the assumption that the crystallization process depends primarily on the coefficient of diffusion of particles and the crystallization and catalyzis rate is directly proportional to the diffusion coefficient. Validity of MNR rule for diffusion phenomena is explained on the basis of the band model of diffusion.

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