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On the conduction mechanism in ionic glasses

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Conduction mechanism in ionic glasses is still considered one of the great challenges in physics and chemistry of glasses [A. Bunde, K. Funke, and M. Ingram, *Solid State Ionics* **105**, 1 (1998)]. We show that consequent application of the routine percolation theory leads to the consistent description of most puzzling conduction effects for both direct current (dc) and alternating current (ac) conductivity. Moreover, comparison of the theoretical results with experimental data reveals the well-known random-energy model suggested a few decades ago for ionic transport in glasses as a very plausible model. The results provide a general basis for the study of transport phenomena in ionic glasses. © 1999 American Institute of Physics. [S0021-9606(99)70440-X]

I. INTRODUCTION

Ionic transport in glasses has been studied experimentally and theoretically for many decades. We will not review here the whole literature on the subject. One can find many useful references in the recent review article of Bunde *et al.*¹ Fascinating effects have been discovered for ionic conduction. One of them is the intriguing mixed-alkali effect (or, more generally, mixed-cation effect), first observed in 1925.² If one alkali oxide is gradually replaced by another in a series of glasses, some physical properties, in particular, the electrical conductivity, vary in an extremely nonlinear manner. For example, the dc conductivity at $T = 150^\circ\text{C}$ of glassy $(1-x)\text{Li}_2\text{O} \cdot x\text{K}_2\text{O} \cdot \text{SiO}_2$ at $x = 0.5$ is about 10^6 less than those of each of the single-component glasses (at $x = 0$ and at $x = 1$).³ Another intriguing effect is the nonlinear dependence of the conductivity on alkali oxide content in single-component systems.⁴ For example, the dc conductivity at 300°C of $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ increases by a factor of approximately 10^6 as the mole fraction of Na_2O is increased from 0.15 to 0.5. In spite of much effort already devoted to account for these very general and pronounced effects, there is still no consensus among researchers not only on the origin of these effects, but even on the very basic mechanism of the ionic conduction in glasses.^{1,5} Nowadays, everybody seems to agree that ionic conduction in glasses, at least in the dc regime and in the ac regime at not too high frequencies, is due to hopping of ions between localized states in the glass matrix.^{1,5} However, the mechanism of such hopping is the subject of many controversies.^{1,5}

The number of publications on the ionic transport in glasses is enormous. Various aspects of this phenomenon have been emphasized, in particular, the role of the glass structure⁶ and the role of the long-range Coulomb potential⁷ on the hopping transport. The combination of these effects has also been discussed.⁸ Among models suggested so far, the dynamic structure model introduced by Bunde, Ingram, and Maass⁵ seems to dominate the literature recently. Their model is based on the assumption that even at temperatures far below the glass transition temperature, essential relax-

ation of the glass structure can occur in a rather short time comparable to the time of the transport hopping processes. The assumption seems questionable. Moreover, according to this model, mostly the dynamic properties of the glass matrix at relatively low temperatures are responsible for the transport effects. It is difficult to bring this model in agreement with the observation that the mixed-alkali effect is absent in ion-exchanged glasses, i.e., in glasses where ions are exchanged at low enough temperatures.⁹

Another class of studies is based on the simultaneous analysis of NMR and conductivity measurements.^{10,11} Although measurements of the NMR spin-lattice relaxation rates probe the local charge-density fluctuations, whereas conductivity measurements probe the long-range diffusion of charges, their simultaneous analysis can throw light on microscopic details of the transport mechanism.¹⁰ Moreover, it is this analysis that first led Svare *et al.*¹¹ to a quantitative description of ionic transport within the percolation approach. Later on, Sen *et al.*¹² successfully used this percolation approach to account for the puzzling mixed-cation effect. Their consideration is based on the percolation theory for hopping over the barriers with distributed heights. This is a specific case of a general random-energy model for ionic transport in glasses discussed by Stevels in 1957,¹³ who has shown qualitatively that such a model provides a natural and general explanation for the mixed-alkali effect and other observed interesting phenomena for ionic conduction. Contrary to the dynamic structure model of Bunde and co-workers, in the model of Stevels, it is assumed that the glass structure is essentially rigid at temperatures below the glass transition and, therefore, the dynamic structural reconstruction cannot contribute much to the transport phenomena at rather low temperatures.

A lot of valuable experimental data have been obtained for the frequency-dependent hopping conductivity (see, e.g., Refs. 1, 10, 14–16, and references therein). In the ac regime, a well-known scaling behavior is usually observed according to which the magnitude of the frequency-dependent ac conductivity $\sigma(\omega)$ is scaled by some combination of parameters including the magnitude of the dc conductivity $\sigma(0)$. In spite

of the well-known analysis¹⁷ which shows that the routine pair model is not able to account for the observed effects, the pair model is still preferred by many experimentalists as the most transparent one. In the detailed analysis of the ac conduction in various electronic and ionic systems, Dyre¹⁷ has chosen the model which assumes that conduction takes place by hopping, where the hopping charge carriers are subject to spatial randomly varying energy barriers. This random-barrier model can be formulated in the way well compatible with the model treated by Svare *et al.*¹¹ and by Sen *et al.*¹² to account for the dc conductivity including the mysterious mixed-alkali effect. Moreover, in the random-barrier model, the frequency-dependent conductivity seems to be determined solely by the dc conductivity that agrees well with experimental data. This model of ionic motion via hopping over barriers with distributed heights has been also successfully used in the analysis of the NMR relaxation.^{11,18}

The percolation approach used so far for description of the dc transport in ionic glasses is rather intuitive. The topology of the percolation path that is known to play an important role for hopping transport¹⁹ has not been taken into account yet. With respect to the ac transport, approaches used so far were mainly based on the continuous time random walk approximation that includes an averaging of hopping times, and also on the effective-medium approximation, known to be not quite suitable for a quantitative description of hopping systems with an exponentially broad distribution of hopping rates.¹⁹ Ionic glasses are plausible candidates to possess such a broad distribution.

The aim of our report is to provide a consequent percolation description for ionic transport in glasses. Most ideas that we discuss below are not new. They have been already expressed in more or less close form in previous publications. However, it is the first time that both ac and dc transport phenomena are described within the same universal percolation approach. This approach allows one not only to account for the observed dependences of the dc and ac conductivity on temperature, concentration of ions, frequency of applied electric field, etc., but also to reveal a general transport mechanism that can be used as the basis for future studies of transport phenomena in ion-conducting glasses. We start in Sec. II with a general discussion of possible hopping models, and on the basis of the comparison between dc and ac conductivities we choose the random-energy hopping model as the most plausible. In Sec. III, percolation theory for dc ionic conductivity is described for the example of the random-barrier model that represents a significant simplification of the random-energy model of Stevels.¹³ In Sec. IV, percolation theory for ac conductivity is applied to the random-barrier model. A description of various transport phenomena in the framework of the general random-energy model is discussed in Sec. V. Concluding remarks are gathered in Sec. VI.

II. MODEL FOR IONIC TRANSPORT IN GLASSES

It is difficult to develop *a priori* a theoretical model for transport phenomena in ion-conducting glasses, because little is known about the spatial structure of the potential that influences the motion of ions.

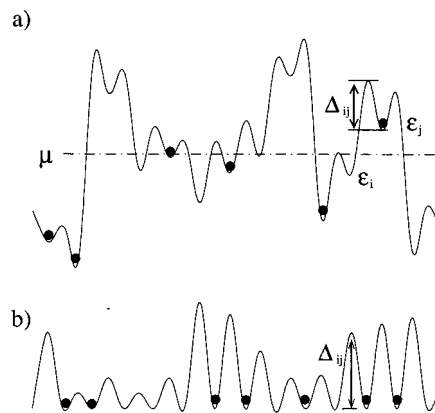


FIG. 1. Potential relief for mobile ions along arbitrary direction in the random-energy model (a) and in the random-barrier model (b).

A possible model for ionic conduction could be the following. One can assume that there are two types of states available for mobile ions in the glass matrix. To the first type belong states that are filled by the modifying ions in the glass production process via cooling from the melt. To the second type belong states that can be occupied by the mobile ions, although they were empty at the glass production. It would seem reasonable to assume that the states of the first type are energetically more favorable for ions than those of the second type, because local surroundings of the localization centers are better adjusted to the presence of modifying atoms. An essential energy gap could exist between the two classes of states. Therefore this model is similar to that for the electronic structure of intrinsic semiconductors with all states in the valence and conduction bands localized. At low enough temperatures, most states in the lower (“valence”) band are occupied by mobile ions and most states in the upper (“conduction”) band are empty. The Fermi level that describes the energy distribution of ions in thermal equilibrium is situated somewhere in the gap region, as is the case in intrinsic semiconductors. In such a system, electric current can be carried only due to thermal excitation of ions over the band gap. Both thermally excited ions in the upper band and vacancies (“holes”) in the lower energy band can serve as current carriers. To move in the upper or in the lower band, the carriers have to overcome energy barriers.

Another simple general model for ionic transport in glasses has been suggested by Stevels.¹³ According to this model, the glass matrix provides a rigid potential relief for mobile ions. An example of such a relief along an arbitrary direction is shown in Fig. 1(a). In their motion through the glass matrix under the influence of the applied electric field, ions have to overcome potential barriers. At low enough temperatures, Fermi level μ is determined by the concentration of mobile ions which occupy the energetically lowest potential wells in the given potential relief. Contrary to the semiconductor model, the energy distribution of localized states for ions is continuous and it possesses no gap. For dc conduction, the largest energy barrier leading to formation of the infinite transport path has to be overcome, while lower barriers are involved in the ac conduction, since only a limited distance has to be traveled in the latter case.

By analyzing just the data for dc conductivity it is not possible to determine which of the models is more suitable to describe ionic transport. It would be possible to account for experimental data on the dc conduction with taking some assumptions in each of these models. However, simultaneous analysis of the dc and ac conductivities excludes the “semiconductor” model. It has been observed in many studies (see, e.g., Ref. 16) that the ac conductivity is much less temperature dependent than the dc conductivity. This observation cannot be explained if the temperature dependence of the conductivity (dc and ac) is determined by the activation of carriers (ions and vacancies) over the broadband gap in the “semiconductor” model. Therefore, we think that this model can be excluded, and one should try to account for experimental observations in the framework of the simple and general random-energy model suggested by Stevels.¹³ Our aim in this report is to develop a quantitative theory of ionic transport within this random-energy model. Such attempts have already been made, though not for the random-energy model, but rather for its simplified version called a random-barrier model. The latter represents a simplification of the random-energy model based on the assumption that only the barrier heights are distributed, while all the wells have the same energy. The corresponding potential relief for mobile ions is illustrated in Fig. 1(b). Svare *et al.*¹¹ and later Sen *et al.*¹² have treated the dc conductivity of ionic glasses within the random-barrier model. We extend below their ideas using a routine percolation approach.¹⁹ This approach takes into account the fractal structure of the percolation cluster neglected in previous considerations. With respect to the ac conductivity, very interesting results for the random-barrier model were obtained by Dyre.^{17,20–22} He used effective-medium and continuous-time random walk approximations and showed that the value of the ac conductivity $\sigma(\omega)$ normalized by the dc conductivity $\sigma(0)$ is a universal function of the reduced frequency $\omega/\sigma(0)$. We apply below a somewhat different percolation approach to the ac conductivity developed by Zvyagin^{23,24} that provides the description of the ac transport in the framework of the same ideas as for the dc transport. Below we first describe the percolation approaches to the dc (Sec. III) and ac (Sec. IV) conductivity in the framework of the random-barrier model, because this model allows one to formulate a rather precise theory. One of the least clear questions in the treatment of the hopping conduction is how to take into account the occupation numbers of localized states used by carriers in their hopping motion.¹⁹ In the random-barrier model, this problem is essentially simplified because in thermal equilibrium, the filling factor of a localized state is simply equal to the fraction x of the states filled by ions. We will exploit this model in the next two sections. Afterwards, in Sec. V, we show that a step toward the random-energy model should be taken in order to account for experimental observations. The extension of the percolation treatment for the random-energy model will be considered. We will not discuss the relation between the random-energy potential relief in the model of Stevels and the glass topology. Such discussions can be found in numerous publications including the initial paper of Stevels.¹³

III. PERCOLATION APPROACH TO THE dc IONIC CONDUCTION IN THE RANDOM-BARRIER MODEL

A quantitative theory for the dc hopping ionic conductivity based on the percolation approach in the framework of the random-barrier model has been recently suggested by Svare *et al.*¹¹ and by Sen *et al.*¹² It has been formulated in the following manner. The potential energy wells in a structurally disordered glass differ in shape from site to site so that ions see a distribution of barrier heights E_b against hops to the next energy well. The hopping rate is related to the height of the barrier as

$$v(E_b) = v_0 \exp\{-E_b/kT\}, \quad (1)$$

where k is the Boltzmann constant, T is the temperature, and $v_0 \approx 3 \cdot 10^{13} \text{ s}^{-1}$ is the attempt-to-escape frequency.¹¹ Some distribution of barrier heights $F(E_b)$ is assumed and the task is to calculate the conductivity. It is convenient to consider localized states for ions as sites of a regular lattice. The dc conductivity is associated with the percolation motion of ions through the low-energy pathways on the lattice. The bottleneck barrier E_c , i.e., the largest barrier to be overcome by ions to establish a continuous path through the system, is determined as

$$P = \int_0^{E_c} F(E) dE, \quad (2)$$

where P is the minimal fraction of barriers that provide the infinite path through the lattice. This fraction is equal to 0.25 in the case of a simple cubic lattice with $z=6$ nearest neighbors.¹⁹ It was suggested¹¹ to calculate the average time between jumps

$$\tau_{av}(T) = P^{-1} \int_0^{E_c} [1/6v(E)] F(E) dE, \quad (3)$$

and to use the following master formula for the dc conductivity:

$$\sigma_{dc} = NP \frac{e^2 d^2}{6kT\tau_{av}}, \quad (4)$$

where N is the concentration of conducting ions, e is the elementary charge, and d is the average hop length between the neighboring potential wells.

This description differs from the routine percolation approach to the hopping transport in a system with exponentially broad distribution of hopping rates. Descriptions of the routine percolation approach can be found already in handbooks.¹⁹ Nevertheless, we find it useful to present here briefly the correct approach aiming at the discussion of the scaling behavior of the ac conductivity in the next section. The result for the exponential term in the temperature dependence of the dc conductivity given by the correct approach does not differ from the dependence given by Eqs. (1)–(4). However, the preexponential factor should be treated more carefully. It is important for us, because in the next section we compare the expressions for ac and dc conductivities in order to discuss the scaling behavior of the ratio $\sigma_{ac}(\omega)/\sigma_{dc}$.

Following Svare *et al.*,¹¹ let us consider a glass matrix as a cubic lattice of localized states for ions separated by po-

tential barriers. Calculation of the dc conductivity in such a system is equivalent to the calculation of the conductivity in a system of random resistances placed between nearest lattice sites. A resistance placed between neighboring localized states i and j has the resistivity

$$R_{ij} = R_0 \exp\{\xi_{ij}\}, \quad (5)$$

where the quantity ξ_{ij} has a broad distribution $F(\xi)$. It is worth noting for further discussion that one should take into account the probabilities of filling of the localized states i and j . In the case of the random-barrier model, the filling probability of any localized state is equal to the fraction x of occupied states. The quantity ξ_{ij} in this model is equal to E_{ij}/kT , where E_{ij} is the energy barrier between states i and j . Percolation threshold ξ_c , is determined analogous to Eq. (2),

$$P = \int_0^{\xi_c} F(\xi) d\xi. \quad (6)$$

One should connect all pairs of states having the values ξ smaller than ξ_c and obtain herewith an infinite percolation cluster. If we further increase ξ from ξ_c to $\xi_c + 1$, the presence of an infinite cluster will cause the conductivity $\sigma(\xi)$ to increase rapidly due to the rapidly diminishing correlation radius of the cluster¹⁹

$$L_c(\xi) = l_0 \alpha (\xi - \xi_c)^{-\nu} \xi_0^\nu \equiv L_{c0} (\xi - \xi_c)^{-\nu}. \quad (7)$$

Here l_0 is the lattice constant, ξ_0 is proportional to the width of the distribution $F(\xi)$, α is a numerical constant, and $\nu \approx 0.9$ is the critical index characterizing the universal topology of the infinite cluster. Further increasing ξ cannot significantly alter $\sigma(\xi)$, even though the density of the infinite network continues to rise.¹⁹ This is because if we increase $\xi - \xi_c$ several times over, we will introduce resistances exponentially larger than $\exp\{\xi_c\}$. The conductivity is described by the formula

$$\sigma_{dc} = \sigma_0 \exp\{-\xi_c\}. \quad (8)$$

For the random-barrier model, this expression takes the form

$$\sigma_{dc} = \sigma_0 \exp\{-E_c/kT\}, \quad (9)$$

that agrees with Eq. (4) with respect to the exponential term for the broad class of distributions $F(E)$. In order to obtain preexponential factor σ_0 , one should perform a more careful analysis¹⁹ that gives for σ_0 , equation

$$\sigma_0 = e^2 v_0 x (1-x) / (kTL_{c0}), \quad (10)$$

where L_{c0} is the value of the correlation radius of the infinite cluster at $\xi = \xi_c + 1$, and x is the fraction of localized states on the lattice occupied by the mobile carriers. Replacing L_{c0} by $L_c(\xi_c + 1)$, one obtains

$$\sigma_0 = e^2 v_0 (l_0 \alpha \xi_0^\nu)^{-1} x (1-x) (kT)^{-1}. \quad (11)$$

Numerical constant α is equal to 1 for the homogeneous distribution¹⁹

$$F(\xi) = \{1/\xi_0 \text{ for } \xi < \xi_0; 0 \text{ for } \xi > \xi_0\}. \quad (12)$$

Comparison between Eqs. (8)–(11) and Eqs. (1)–(4) shows that the routine percolation approach¹⁹ gives for σ_{dc} a some-

what different result compared to that obtained in Refs. 11 and 12, although the exponential term in the temperature dependence of the dc conductivity has the same form $\sigma_{dc} \propto \exp\{-E_c/kT\}$. The length scale decisive for transport in the percolation theory is the correlation length of the infinite cluster L_c and not the distance between the neighboring sites d . Precise definition of L_c can be found in handbooks.¹⁹ Roughly speaking, L_c is of the order of the typical distance between the critical resistances with $\xi \approx \xi_c$. It is this distance that determines the transport length corresponding to the critical hopping time $t_c \sim v_0^{-1} \exp\{E_c/kT\}$ because hops over barriers with heights smaller than E_c are exponentially faster than critical hops with t_c . Qualitatively, percolation reminds diffusion with characteristic time t_c and characteristic length L_c . The total concentration of carriers N is usually much larger than L_c^{-3} , because L_c diverges in the vicinity of the percolation threshold. Under such circumstances, concentration of carriers that instantly contribute to transport is of the order of L_c^{-3} . Combining these estimates, one comes to the combination of parameters given by Eqs. (9) and (10), where the factor $x(1-x)$ accounts for occupation of the states participating in the critical transitions and L_c is replaced by L_{c0} because the effective percolation cluster corresponds to $\xi = \xi_c + 1$. Qualitative arguments above are given for illustration. Precise derivation of Eqs. (5)–(11) can be found elsewhere.¹⁹ It is also worth noting that neither the geometrical structure of the percolation cluster, nor the value of critical index ν depend on the distribution function of barrier heights $F(kT\xi_{ij})$. Parameter α does depend on this distribution, being a numerical constant of the order unity.¹⁹

In the random-barrier model illustrated in Fig. 1(b), the activation energy of the dc conductivity is equal to the energy difference between the percolation level and the level of the isoenergetic potential wells that can be occupied by ions. This model has been successfully used recently to account for the intriguing mixed-cation effect.¹² If one assumes that the number of hopping sites for ions of each modifier is essentially reduced due to the presence of the second modifier, the number of effective neighbors on the lattice should also be reduced, leading to the increase of the percolation number P in Eq. (6). This causes an increase of the percolation level $E_c = kT\xi_c$ that should be identified with the activation energy E_a in the expression

$$\sigma_{dc} \propto \exp\{-E_a/kT\}. \quad (13)$$

The most intriguing effect of glasses with a single modifier is the extremely nonlinear dependence of the dc conductivity on the concentration of the modifying ions x . It has been well established that the effect of the concentration x on the conductivity is via the activation energy E_a in the exponential temperature dependence of the conductivity⁵ described by Eq. (13). In the percolation description given above, the activation energy E_a should be identified with the percolation level E_c . In order to explain the observed decrease of E_a with increasing x in the framework of this model, one has to assume that the distribution $F(E_b/kT)$ of barrier heights changes so much that it accounts for the decrease of E_c with increasing x . For the case of the uniform distribution described by Eq. (12) that would imply a shrink-

age of the distribution width $E_0 = kT\xi_0$. There are no doubts that the glass structure can change with changing concentration of ions x . However, it is not clear why the barrier heights should be affected by the concentration of ions exactly in the way necessary to account for the observed strong nonlinearity of the dc conductivity $\sigma(x)$. In Sec. V, we show that a more general random-energy model is a better candidate to account for this effect and also for the mixed-alkali effect.

IV. PERCOLATION APPROACH TO THE ac IONIC CONDUCTION IN THE RANDOM-BARRIER MODEL

A lot of publications are devoted to the experimental study of ac ionic conduction in glasses, although the main features were already established by the end of the 1950s.^{13,25–27} Their summary can be found, e.g., in Ref. 17, and we do not specify all of them here. Many cases of conductivity curves shifted in frequency of the applied field ω and temperature T to coincide have been reported in the literature. Recently, another observation of the universal scaling behavior of the ac conductivity $\sigma_{ac}(\omega)$ has been made.¹⁶ $\sigma_{ac}(\omega)$ is a function of three independent variables: ω , x , and T , where x is the mole fraction of the network modifier. It was shown¹⁶ that $\sigma_{ac}(\omega, x, T)$ has a remarkably simple scaling behavior,

$$\sigma_{ac}(\omega, x, T) / \sigma_{dc} = f(\omega x / \sigma_{dc} T), \quad (14)$$

which in a direct way includes the dependence on the modifier content x in the dispersion relation. This scaling behavior shown explicitly for $x\text{Na}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ glass was considered to be a challenge for hopping theories.¹ However, this universality should not be too surprising for followers of random-barrier theories, where $\sigma_{dc} \propto x/T\tau_{av}$ so that σ/σ_{dc} is a universal function of $\omega\tau_{av}$. Our aim in this report is to show that this scaling relation is also consistent with the hopping theory for ionic transport in glasses in its most general formulation.

Theoretical models for ac conduction in hopping systems have already become a subject of many review papers, among which the reviews of Long²⁸ and Dyre¹⁷ seem to be most complete. Therefore, we remark very briefly on these models here in order to justify our choice of the working model for ac ionic conduction in glasses. For a long time, the pair approximation (PA) introduced in 1961 by Pollak and Geballe²⁹ was considered as the only reliable theory for the frequency-dependent conductivity. In the PA, the total ac response is given by the sum of the individual responses of pairs of sites distributed at random through the material. The response of a hopping system in the full frequency range was usually assumed to be the sum of the dc and PA results. This description is unable to account for the ac conductivity at moderate frequencies at which the dominant contribution to the conductivity comes from the clusters containing more than two sites. In real hopping systems, different characteristic clusters determine current at different frequencies ω . At $\omega=0$, the infinite percolation cluster provides the current path. With increasing ω , clusters of smaller size dominate the current and only at very large ω , the PA is suitable to describe the frequency-dependent conduction. Unfortunately,

the PA is still used by experimentalists in their attempts to account for experimental data in a broad frequency range including rather low frequencies.

Three classes of models have been suggested for the intermediate frequency regime between very low frequencies, at which conduction has the dc character, and very high frequencies, at which the PA should be valid. The first class of models is based on various modifications of the PA. Most popular have become the “effective-medium models,”³⁰ and the “extended pair approximation,”³¹ in which the disordered hopping medium surrounding a particular pair of sites is replaced either by a uniform effective medium, or by a simple equivalent circuit whose properties may be adjusted self-consistently by some averaging procedure. Being able to account for some experimental observations, these models seem to miss the very basic physics of the problem, namely, the interplay between contributions of clusters with different sizes at different frequencies. The second class of hopping models for the ac conduction contains the models based on the continuous-time random-walk (CTRW) approximation (see, e.g., Ref. 17 and references therein). The CTRW always includes some averaging procedure for hopping times, and it is difficult to justify such an approach.³² Moreover, the CTRW is known to give a wrong estimate for dc conductivity by several orders of magnitude.¹⁷ The third class of models is the cluster models, which are based on consideration of finite clusters contributing to the ac conductivity at various frequencies. These are undoubtedly most consequent models. According to the percolation theory, they presume that conduction in the dc regime is determined by the infinite cluster constructed from sites which provide a connected path for carriers through the whole system with the easiest hopping transitions. With increasing frequency of the applied electric field, there is no necessity for carriers to penetrate through the whole system, and the clusters that determine the ac response become smaller in size. In the limit of the very high frequencies, the PA must come in play. Cluster theories for ac conduction in hopping systems were developed by several groups.^{23,24,33,34} While the theory of Böttger *et al.*³³ was developed for the so-called r -percolation problem suitable to describe tunneling motion of carriers (electrons), the theory of Zvyagin^{23,24} can be easily used to describe also the hopping motion of ions. Therefore, we use below the approach suggested by Zvyagin to account for the scaling behavior of $\sigma_{ac}(\omega, x, T)$. We present below in detail some of Zvyagin’s ideas, because most of them have been only published in Russian²⁴ and only a brief summary is available in English.²³ We start with analysis of the random-barrier model illustrated in Fig. 1(b) and show that such a model does not provide precisely enough the scaling parameter observed experimentally. Therefore one should consider a more general random-energy model illustrated in Fig. 1(a).

In the ac regime, ions move over finite distances, and in order to calculate the conductivity, one has to find the optimal paths for the shift of ions under the influence of external field F during finite time t . Zvyagin has invented the following percolation approach to this problem. Due to the exponentially broad distribution of the hopping rates

$$\Gamma = \Gamma_m \exp\{-\xi\}, \quad (15)$$

for different pairs of neighboring sites, caused by the broad distribution of exponents ξ , one can distinguish between the clusters that include only sites with fast transition rates between neighbors $\Gamma > \Gamma_t$ from clusters including slower transition rates $\Gamma < \Gamma_t$, the threshold rate Γ_t being determined by the condition²⁴

$$\Gamma_t \approx \tau^{-1}, \quad (16)$$

where τ is the relaxation time in finite clusters dominating the conductivity at $t \approx \tau$. The preexponential factor Γ_m for the random-barrier model has the form²⁴

$$\Gamma_m = x(1-x)v_0, \quad (17)$$

where v_0 and x are the same as in Eq. (10).

In order to calculate ac conductivity $\sigma(\omega)$, one can use the routine procedure with first calculating the step transient response of the system to the switching on/off of a constant electric field F at $t=0$ and using afterward the Fourier transformation. At time t , quasiequilibrium is established in clusters which contain only transitions with rates $\Gamma > \Gamma_t$, while clusters which contain sites with lower transition rates between neighbors cannot yet respond to the applied electric field. At each moment t , the clusters that have responded to the external field can be considered as isolated, because they are connected to the rest of the system via transitions with rates much lower than Γ_t . Since the problem is reduced to consideration of isolated quasiequilibrium clusters, the calculation of the transient current [and hence, the calculation of the frequency-dependent conductivity $\sigma(\omega)$] can be carried out straightforwardly.

The current density is determined by equation

$$j = (1/V) \frac{d}{dt} \sum_r D_r, \quad (18)$$

where V is the volume of the system and the sum is taken over all quasiequilibrium clusters, D_r being the dipole moment of the cluster number r ,

$$D_r = e \sum_i l_i f_i. \quad (19)$$

Here l_i is the projection of the radius vector of the site i onto the field direction and f_i is the equilibrium filling factor of this site with taking into account the applied electric field F . The field-dependent part of the dipole moment D_r is²⁴

$$D_r(F) = s_r L_r^2 \bar{C}_r F, \quad (20)$$

where s_r is the number of sites in the cluster, L_r is the cluster length, and \bar{C}_r is determined as

$$\bar{C}_r = \frac{e^2}{kT} s_r^{-1} L_r^{-2} \sum_i l_i^2 f(\varepsilon_i) [1 - f(\varepsilon_i)], \quad (21)$$

where $f(\varepsilon_i)$ is the equilibrium occupation number of site i with energy ε_i and the summation is over all sites i belonging to the cluster. In the random-barrier model, $f(\varepsilon_i) = x$. In Eq. (18), the sum can be taken over the cluster sizes s ,

$$j = \frac{d}{dt} \sum_s n(s) D(s) = \frac{d}{dt} \sum_s s n(s) \bar{C} L^2(s) F, \quad (22)$$

where $n(s)$ is the concentration of clusters with size s , and \bar{C} is assumed independent of the cluster size. It can be easily shown¹⁹ that the sum in Eq. (22) is determined by clusters with sizes close to the critical size s_c , because for $s \ll s_c$, the concentration of clusters $n(s)$ decreases with increasing cluster size slower than the increase of the product $L^2(s)s$, while for $s \gg s_c$, the concentration $n(s)$ decreases much faster than the increase of the product $L^2(s)s$. Therefore, $L(s)$ can be approximated by the critical length determined by Eq. (7). Assuming that critical clusters fill the volume of the system by the dense distribution, one can estimate their concentration as $n(s_c) \sim L_c^{-3}$. The number of sites in the critical cluster is determined by the scaling relation¹⁹

$$s_c = [(\xi_c - \xi)/\xi_0]^{-\Delta}, \quad (23)$$

where ξ_0 is the characteristic scale of the distribution function of ξ . Using Eqs. (7) and (23), one obtains the equation for the current density,

$$j \cong \frac{\bar{C}}{L_c^3} F \xi_0^\Delta \frac{d}{dt} (\xi_c - \xi)^{1-\zeta}, \quad (24)$$

where Δ and $\zeta = \Delta - \nu + 1$ are the critical indices with values $\Delta \cong 2.2$, $\zeta \cong 2.3$ in three-dimensional (3D) systems.¹⁹

Consider, following Zvyagin,²⁴ the clusters that determine at time t the system response to the steplike switching of the electric field. Each of such clusters can be considered as consisting of two parts I and II connected by a key bond with the slowest transition rate Γ for the chosen cluster. Under the influence of the external field, the carriers in the cluster are redistributed between these two parts. The quantity of interest is the change δn_I of the quasiequilibrium number of carriers in part I due to the influence of the external field F . Condition $\delta n_I = -\delta n_{II}$ is fulfilled. The quasiequilibrium state after the application of the electric field is established in the cluster at times much shorter than the time of transitions connecting the cluster to the rest of the system. Considering explicitly the filling factors of all cluster sites in regions I and II before and after the application of the external field, one can develop the equation that describes the time evolution of δn_I after the constant electric field is turned off,²⁴

$$\frac{d\delta n_I}{dt} = -\frac{\delta n_I}{\tau}, \quad (25)$$

where

$$\tau = \frac{kT}{e^2} C/\Gamma, \quad (26)$$

$$C^{-1} = C_I^{-1} + C_{II}^{-1}, \quad (27)$$

$$C_{I(II)} = \frac{e^2}{kT} \sum_i f(\varepsilon_i) [1 - f(\varepsilon_i)], \quad (28)$$

the sum being taken over all sites i belonging to the corresponding part of the cluster. One can conclude that the relaxation time of charge carriers in a finite cluster is equal to

the time constant of the equivalent circuit consisting of the key resistance and two capacitances connected sequentially to both sides of the resistance.²⁴ If $C_I \sim C_{II}$, the capacity of the equivalent circuit is of the order of cluster capacity that is proportional to the number of cluster sites: $C \sim C_0 s$, where C_0 is the cluster capacity per site. It is, however, not necessary that capacities of parts I and II are equal to each other. If these capacities are different, the total capacity of the cluster C responsible for the relaxation time τ in Eq. (26) is determined by the minimal of C_I and C_{II} as described by Eq. (27). Therefore, the numerical value of C can be much less than $C_0 s$. We account for this by introducing a numerical coefficient β ,

$$C = \beta C_0 s. \quad (29)$$

We do not know how to determine the value of β by theoretical calculations and therefore we will use this constant as a fitting parameter for comparison with experimental data. One should just have in mind that β can be much less than unity.

The key transition in a finite cluster, which determines the system response at time t , has the rate $\Gamma(t)$ related to the percolation exponent ξ as²⁴

$$\ln \frac{\Gamma(t)}{\Gamma_c} = \xi_c - \xi, \quad (30)$$

where

$$\Gamma_c = \Gamma_m \exp\{-\xi_c\}. \quad (31)$$

At time t , clusters with $\tau \cong t$ are responsible for the transient current. Using Eqs. (23), (26), and (29)–(31), we obtain for $\Gamma(t)$,

$$\Gamma(t) \ln \frac{\Gamma(t)}{\Gamma_c} = \frac{\beta C_0 \xi_0^{\Delta} kT}{te^2}. \quad (32)$$

Introducing Eq. (30) into Eq. (24) and assuming $\bar{C} \approx \beta C_0$, one obtains²⁴ the equation for the current density,

$$j = \frac{\sigma_0}{\Gamma_m} \Gamma F, \quad (33)$$

where Γ is determined by Eq. (32) and σ_0 is given by Eq. (10). Fourier-transforming Eqs. (32) and (33), one obtains the frequency-dependent conductivity²⁴

$$\sigma(\omega) = \sigma_0 \Gamma(\omega) / \Gamma_m, \quad (34)$$

where Γ is determined by the equation

$$\Gamma(\omega) \ln \frac{\Gamma(\omega)}{\Gamma_c} = \omega \beta C_0 \xi_0^{\Delta} kT / e^2. \quad (35)$$

The above derivation of $\sigma(\omega)$ is valid for the frequency range^{23,24}

$$\Gamma_c \ll \omega \ll \Gamma_m, \quad (36)$$

because for frequencies out of this range, clusters that determine response become either too large (at $\omega \sim \Gamma_c$) and the variation of the minimum transition rate with time becomes nonexponential, or they are too small (at $\omega \sim \Gamma_m$) to be treated in terms of the average cluster capacity. Frequency

range corresponding to condition (36) is extremely broad. Obtained expressions (34)–(35) give the correct dc value $\sigma(0)$.

It is clearly seen from Eqs. (34) and (35) that the ratio $\sigma(\omega) / \sigma_{dc}$ is a universal function of parameter

$$A = \frac{C_0 \omega \xi_0^{\Delta} kT}{\Gamma_c e^2}. \quad (37)$$

Using Eqs. (8), (10), (17), and (31), one can rewrite A as

$$A = \left(\frac{\omega}{\sigma_{dc} kT} \right) \frac{C_0 \xi_0^{\Delta} kT}{L_{c0}} \equiv \left(\frac{\omega}{\sigma_{dc} kT} \right) \Lambda. \quad (38)$$

Let us now consider the dependences of parameter

$$\Lambda = \frac{C_0 \xi_0^{\Delta} kT}{L_{c0}} \quad (39)$$

on temperature and on the concentration x of mobile ions in the framework of the random-barrier model. According to Eqs. (28) and (29), this model gives

$$C_0 = \frac{e^2}{kT} x(1-x). \quad (40)$$

Hence, parameter Λ is equal to

$$\Lambda = \frac{\xi_0^{\Delta} e^2}{L_{c0}} (x - x^2). \quad (41)$$

Temperature dependence of L_{c0} is determined via Eqs. (7) by the temperature dependence of $\xi_0 = E_0 / kT$, E_0 being the width of the distribution of barrier heights in the random-barrier model,

$$L_{c0} \propto \xi_0^{\nu}. \quad (42)$$

At $x \ll 1$, these expressions give the relation for Λ ,

$$\Lambda \propto x(kT)^{\nu-\Delta}. \quad (43)$$

Experimental data¹⁶ evidence the scaling parameter $\omega x / (\sigma_{dc} kT)$ for the ratio $\sigma(\omega) / \sigma_{dc}$. While x -dependence of Λ agrees well with this observation, T -dependence deviates from the experimental one. Λ should be independent of temperature in order to account for experimental data. Equation (42), obtained above for the random-barrier model, gives $\Lambda \propto (kT)^{\nu-\Delta} \equiv (kT)^{-1.3}$ and, therefore, it cannot account for the observed scaling behavior of $\sigma_{ac}(\omega, x, T) / \sigma_{dc}$. In the next section, we consider a more realistic random-energy model and show that this model can account not only for the scaling behavior of $\sigma_{ac}(\omega, x, T) / \sigma_{dc}$, but also for the fascinating effects observed for σ_{dc} .

V. PERCOLATION APPROACH TO THE ac AND dc IONIC CONDUCTION IN THE RANDOM-ENERGY MODEL

The random-barrier model considered above is very convenient to treat ionic conduction within the percolation approach. However, it was shown in Secs. III and IV that it fails to account for the strong nonlinear dependence of the dc conductivity on the concentration of mobile ions and also for the correct scaling behavior of $\sigma_{ac}(\omega, x, T) / \sigma_{dc}$. Therefore, a more realistic random-energy model should be considered.

The latter is the natural extension of the random-barrier model in the sense that not only the barrier heights, but also the energies of potential wells are considered to be distributed. It brings considerable complications to the theoretical treatment. In the random-barrier model, filling factors of localized states are determined solely by the fraction x of mobile ions. In the random-energy model these filling factors depend also on the energies of localized states.

We start our analysis with the dc conduction. First, we formulate and solve the problem in a semiquantitative way and afterward we formulate a precise percolation approach. As has been mentioned in the Introduction, there are two most pronounced effects related to the dc ionic conduction in glasses. One is the extremely nonlinear dependence of σ_{dc} on fraction x of modifying ions in the single-modifier glasses and the other one is the mixed-alkali effect. We start with the nonlinearity for the single-modifier case.

It has been well established⁵ that the nonlinear dependence of σ_{dc} on x is caused by the strong dependence of the activation energy of σ_{dc} on x . Based on the analysis of experimental data, it has been shown⁵ that activation energy E_a for the dc conductivity logarithmically depends on x ,

$$E_a(x) \propto \ln(1/x). \quad (44)$$

In the framework of the random-energy model, the activation energy is equal to the energy difference between the percolation level E_c and the Fermi energy μ . If we assume that the percolation level is determined solely by the potential relief of the barriers and that this relief is not influenced drastically by the change of x , the dependence of E_a on x is determined by the x -dependence of the Fermi energy $\mu(x)$. In order to determine the latter, it is necessary to know the distribution $g(\varepsilon)$ of energies ε of localized states (DOS). Of course, the above assumption on the independence of the potential relief on the concentration x of mobile ions is plausible only at rather low concentrations x . Nevertheless, we consider the glass structure independent of x in the whole range of ion concentrations just as a model. Ions in thermal equilibrium fill the deepest potential wells, i.e., the tail states of the DOS with lowest possible energies. Assume the simplest exponential shape for this tail,

$$g(\varepsilon) = \frac{1}{\varepsilon_0} \exp\{\varepsilon/\varepsilon_0\}, \quad (45)$$

with characteristic energy ε_0 . The dependence of the Fermi energy on the fraction x of localized states occupied by mobile ions can be estimated via relation

$$x \cong \int_{-\infty}^{\mu} g(\varepsilon) d\varepsilon. \quad (46)$$

Using Eqs. (45) and (46), and identifying E_a with $E_c - \mu(x)$, one obtains the logarithmic dependence

$$E_a \cong E_c + \varepsilon_0 \ln(1/x), \quad (47)$$

that accounts for the strong nonlinear x -dependence of σ_{dc} ,

$$\sigma_{dc} \propto \exp\left\{-\frac{E_a}{kT}\right\} \propto (x)^{\varepsilon_0/kT}. \quad (48)$$

By the appropriate choice of the DOS function $g(\varepsilon)$, one can obviously account for experimentally observed nonlinear dependence $\sigma_{dc}(x)$.

We present below a precise formulation of the percolation problem within the random-energy model for a single-alkali glass. It is rare that a percolation problem can be formulated in such an accurate form. This accuracy is provided by the rather simple mechanism of ionic hopping. Ions use only the nearest localized states for their hops and they do not tunnel to more distant sites. This excludes the spatial factor from the formulation of the percolation problem and allows one to consider only energetic factors, such as the energies of the initial and final localized states and also the height of the barrier to be overcome.

Let us assume that localized states have DOS $g(\varepsilon)$ and the barriers Δ (above the highest of the two localized states involved in a hop) have the distribution $F(\Delta)$. The definition of Δ is illustrated in Fig. 1. If transitions occur via interactions with phonons, one can show¹⁹ that local resistances between neighboring sites i and j have the form

$$R_{ij} = R_0 \exp\left\{\frac{\varepsilon_{ij} + \Delta_{ij}}{kT}\right\}, \quad (49)$$

where

$$\varepsilon_{ij} = (1/2)\{|\varepsilon_i - \varepsilon_j| + |\varepsilon_i - \mu| + |\varepsilon_j - \mu|\}. \quad (50)$$

The percolation problem is formulated in the following way. Let us introduce some small numerical constant ξ and consider all bonds in the system with $(\varepsilon_{ij} + \Delta_{ij})/kT \leq \xi$. The value ξ will be progressively increased until at $\xi = \xi_c$, an infinite percolation cluster is formed from the pairs of sites corresponding to this inequality. The exponent of the dc conductivity is equal to ξ_c .¹⁹ Assuming, for simplicity, that localized states for ions form a regular lattice, one can determine the value of ξ_c via equation

$$P = \int_0^{\xi_c kT} F(\Delta) \left\{ \int_{\mu}^{\mu + \xi_c kT - \Delta} g(\varepsilon_i) \int_{\varepsilon_i - \xi_c kT + \Delta}^{\mu + \xi_c kT - \Delta} g(\varepsilon_j) d\varepsilon_j d\varepsilon_i + \int_{\mu - \xi_c kT + \Delta}^{\mu} g(\varepsilon_i) \int_{\mu - \xi_c kT + \Delta}^{\varepsilon_i + \xi_c kT - \Delta} g(\varepsilon_j) d\varepsilon_j d\varepsilon_i \right\} d\Delta, \quad (51)$$

where P is the fraction of nonbroken bonds of the lattice corresponding to the percolation threshold. Fermi level μ can be determined via Eq. (46). Using an exponential function determined by Eq. (45) for $g(\varepsilon)$ and a Gaussian function for $F(\Delta)$,

$$F(\Delta) = (1/\sqrt{2\pi\sigma_\Delta^2}) \exp\{-(\Delta_0 - \Delta)^2/2\sigma_\Delta^2\}, \quad (52)$$

and assuming that localization sites form a cubic lattice with $P=0.25$, one obtains for the activation energy of the dc conductivity, dependences $E_a(x)$ shown in Fig. 2. Values $\Delta_0=0.35$, $\Delta_0=0.26$, and $\sigma_\Delta=0.15$ eV were assumed to obtain these data. Experimental data for the glass $x\text{Na}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ are also shown in this figure as taken from Refs. 1 and 5. Good agreement between theoretical results and experimental data can be concluded for $\varepsilon_0 \approx 0.6$ eV. The density of states' function determined by Eq. (45) is taken just for simplicity. It is very encouraging that even such a simple choice of the DOS function allows one to account for the

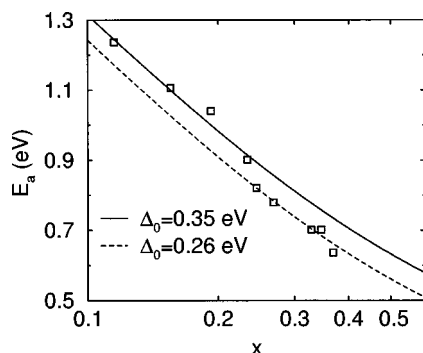


FIG. 2. Activation energies of the dc conductivity calculated via Eq. (51) for DOS determined by Eq. (45) with $\varepsilon_0 = 0.6$ eV and distributions of barriers determined by Eq. (52) with $\Delta_0 = 0.35$ eV (solid line) and $\Delta_0 = 0.26$ eV (dashed line). Experimental data taken from Refs. 1 and 5 are shown by squares.

puzzling effect^{1,5} using a routine formulation of the percolation theory. It is also interesting whether or not the parameters of the system are reasonable that are needed to account not only for the activation energy E_a of the dc conductivity in Fig. 2, but also for the magnitude of the conductivity, i.e., for the preexponential factor σ_0 in Eq. (8). In the random-barrier model, σ_0 is determined by Eq. (11), where α is the numerical parameter equal to unity for uniform distribution of barriers. One can show using Eqs. (8), (45), (46), (51), and (52) that for the random-energy model, σ_0 is determined by an expression analogous to Eq. (11),

$$\sigma_0 = e^2 v_0 (l_0 \alpha \xi_0^v)^{-1} (kT)^{-1}, \quad (53)$$

where $\xi_0 = 2\varepsilon_0/kT$ and α is the numerical parameter of the order unity.¹⁹ Note that the fractional concentration of ions x in this model determines the quantity ξc in Eq. (8) via the Fermi level μ as in Eq. (46) and x does not appear in the preexponential factor σ_0 . Taking experimental data for σ_{dc} in the glass $x\text{Na}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ from Ref. 16, and assuming for parameters ε_0 and α the values 0.6 eV and 1, respectively, one obtains that in order to fit experimental values of σ_0 at different temperatures, the value of the ratio $v_0/l_0 \approx 10^{21}/\text{s/cm}$ is needed. Taking for attempt-to-escape frequency the value¹¹ $v_0 \approx 3 \cdot 10^{13} \text{ s}^{-1}$, one obtains for the distance between neighboring sites for ions in the glass matrix $l_0 \approx 3 \cdot 10^{-8} \text{ cm}$. This shows that the percolation approach gives even a rather reasonable magnitude of the dc conductivity.

Concerning another puzzling effect related to the mixed-alkali behavior, its qualitative explanation in the random-energy model has been already given by Stevels.¹³ It is assumed that in the random glass structure, ions of different sizes can be incorporated more easily, geometrically, than ions all of one size (see also Ref. 35). Hence, the energy of binding is greater, and the Fermi level μ is lower in the mixed-alkali system compared to the single-alkali one. The activation energy E_a is determined as $E_c - \mu$ and it is larger for the mixed system, provided the structure of barriers and the value of E_c have not drastically changed compared to the single-alkali glass. It is implicit in the random-energy model that the binding energy of an alkali ion to its site varies considerably from site to site and that conductivity is deter-

mined by the least firmly held ions (those with equilibrium energies in the vicinity of μ). Starting with a single alkali glass, as another alkali is substituted, the least firmly held ions in places of geometrically unsatisfactory configuration will be replaced first, the new alkali ion of different size enabling the region to be reconstructed to give a firmer binding. The greatest effect is achieved by the greatest difference in ionic sizes, and the effect is rather symmetrical insofar as it is equally effective for a few small ions amongst large ions as for a few large ions amongst small ions.³⁵ This qualitative explanation seems very reasonable. It speculates solely on the change of the Fermi level μ due to the replacement of some amount of cations A by cations B in the glass matrix. However, within such a model, it is difficult to account for the known experimental result that shows the increase of the activation energy E_a of the dc conductivity due to such a replacement larger than the increase of E_a in a single-cation glass caused by reduction of the number of cations by the same amount as in the case of replacement.³⁵ This experimental result can be well accounted for by the increase of the percolation level E_c in the mixed system due to blockage of sites available for ions A by ions B and vice versa. This effect has been considered in detail by Sen *et al.*¹² Moreover, Sen *et al.* have shown that it is possible to fit perfectly experimental data on the mixed cation effect for various glasses within such an approach. Our approach differs from that of Sen *et al.* by additional distribution of potential wells $g(\varepsilon)$ and hence it is even more rich on unknown fitting parameters. If one assumes the distribution $g(\varepsilon)$ as a δ -function, one comes to the description of Sen *et al.* Therefore there is no doubt that if one allows functions $F(\Delta)$ and $g(\varepsilon)$ in Eq. (51) to change with cation mixing, it is possible to fit experimental results. We will try to study this problem in the future, and at the present stage we would like just to illustrate that Eq. (51) predicts the strong mixed-cation effect even under the very simple assumption that functions $F(\Delta)$ and $g(\varepsilon)$ are constant.

As has been pointed out by many researchers (see, e.g., Refs. 1 and 36), there is a strong site preference for ions A and B in the mixed systems. If cations $A(B)$ cannot occupy the sites occupied by cations $B(A)$ in the glass production by cooling from the melt, the number of available nearest neighbors for hopping of each kind of cations is reduced in the presence of other cations. This effect has been taken into account quantitatively by Sen *et al.*¹² within the random-barrier model in the approach based on the averaging of hopping times. The decrease in the number of available hopping sites in the mixed-cation glass compared to the single-modifier system has been chosen to fit the spin-lattice relaxation times.¹² We perform a numerical quantitative calculation of the dc conductivity in the mixed-cation glass within the percolation approach. The fractions of ions A and B are x_A and x_B , respectively. We assume that sites occupied in the glass production by ions B are inaccessible for ions A , and vice versa. Sites that are empty during the cooling of the glass from the melt can be used by both kinds of ions for their hopping motion. Since the fraction x_B of sites is not accessible for ions A , their density of states is reduced to $(1 - x_B)g(\varepsilon)$, where $g(\varepsilon)$ is the DOS of ions A in the single-

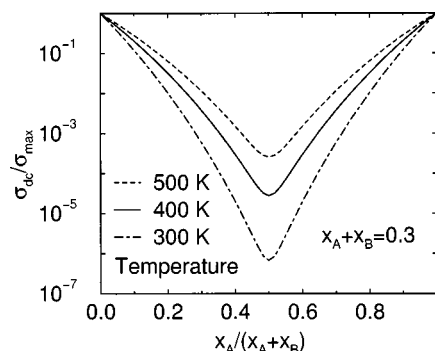


FIG. 3. Normalized dc conductivity in the mixed A-B system as a function of the relative concentration of ions A at different temperatures. The fraction of states occupied by ions A and B is equal to 0.3.

cation glass. According to Eq. (51), in order to determine the percolation level for ions A in the mixed system, one has to solve this equation replacing P with $P_A = P/(1-x_B)^2$. The percolation level for ions B is determined by the solution of the similar problem with replacing P with $P_B = P/(1-x_A)^2$. In Fig. 3, we show the results of numerical calculations of σ_{dc} for the mixed system obtained with Eq. (51), where P is replaced by either P_A or P_B depending on the most efficient cations with respect to their contribution to the conductivity. For calculations we used $g(\varepsilon)$ determined by Eq. (45) with $\varepsilon_0 = 0.6$ eV and $F(\Delta)$ determined by Eq. (52) with $\Delta_0 = 0.35$, $\sigma_\Delta = 0.15$ eV. In our description we assume that the glass structure does not change with changing the composition in replacing one kind of ions by another one, as expressed in the fixed functions $g(\varepsilon)$ and $F(\Delta)$ in Eq. (51). This is similar to the model assumption of the constant glass structure with respect to the ion concentration x in glasses with a single modifier. If such a simple model within the routine percolation approach accounts for the order-of-magnitude value of the effect, it is very plausible that the general description is correct and the mechanism of ion motion is considered appropriately. One can try to fit experimental curves in all details by adjusting distribution functions $g(\varepsilon)$ and $F(\Delta)$ for different compositions of ions. Our aim in this report is not to fit experimental curves, but rather to show that it is possible to account for the puzzling and challenging effects^{1,5} within the simplest random-energy model using the routine theoretical approach.

We would like to emphasize the difference between our approach and the one suggested by Maass *et al.*³⁶ In our approach, the preference of sites for ions A(B) is determined in the glass production, whereas in the model of Maass *et al.*,³⁶ essential dynamic relaxation at rather low temperatures is assumed. Qualitative agreement between theoretical results and experimental data in Figs. 2 and 3 shows that this latter assumption is not necessary. Moreover, our approach accounts for the absence of the mixed-cation effect in systems where cations are exchanged at rather low temperatures.⁹ The dynamic relaxation model fails to account for this effect.

Let us now discuss the percolation description of the ac ionic transport within the random-energy model. It is necessary to modify the theory described in Sec. IV with taking

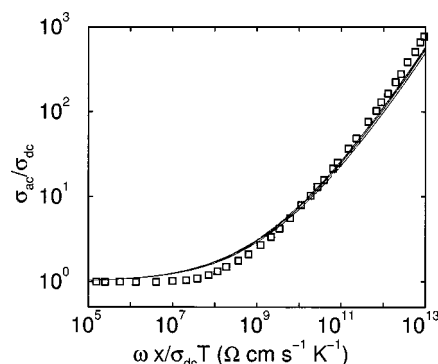


FIG. 4. The ratio $\sigma_{ac}(\omega, x, T)/\sigma_{dc}$ as a function of parameter $\omega x/(\sigma_{dc} k T)$. Theoretical results are shown by solid lines for various values of x and T specified in the text. Experimental data taken from Ref. 16 are shown by squares.

into account the different filling factors of localized states at different energies ε . There are two quantities essentially dependent on the filling factors of localized states. The first one is the transition rate Γ determined as the number of transitions per second between two localized states. The second one is the cluster capacity per site C_0 . It can be shown²⁴ that modifications of Γ do not lead to modifications of the scaling parameter Λ compared to the random-barrier model, since these modifications should be done for both Γ and Γ_c and only the ratio Γ/Γ_c is important. What concerns the modification of capacity C_0 , it should be taken into account explicitly.

It is convenient to replace the summation over cluster sites in Eq. (28) by integration over site energies. Using Eq. (28), one obtains

$$C_0 = \frac{e^2}{kT} \int_{\text{cluster}} f(\varepsilon)[1-f(\varepsilon)]g(\varepsilon)d\varepsilon. \quad (54)$$

Assuming that thermal equilibrium is established, one can use the equilibrium Fermi function $f(\varepsilon)$ in Eq. (54). Since the quantity $f(\varepsilon)[1-f(\varepsilon)]$ is an exponentially decreasing function of the parameter $|\varepsilon - \mu|/kT$, the main contribution to C_0 comes from sites with energies close to the Fermi level μ in the region $|\varepsilon_i - \mu| \leq kT$. The number of such sites is proportional to kT . Therefore, C_0 is approximately independent of T . If the DOS function $g(\varepsilon)$ is steep enough to assume that most of the carriers are situated in localized states with energies close to Fermi energy μ , one obtains $C_0 \propto x$. This gives for the scaling parameter A , expression

$$A = \left(\frac{\omega}{\sigma_{dc} k T} x \right) \Lambda_1, \quad (55)$$

where Λ_1 depends on T very slightly: $\Lambda_1 \propto (kT)^{\nu-\Delta+1} \approx (kT)^{-0.3}$. In Fig. 4, theoretical curves for $\sigma_{ac}(\omega, x, T)/\sigma_{dc}$ are shown for different concentrations x ($x = 0.1; 0.2; 0.3; 0.4$), and temperatures T ($T = 300; 400; 500; 600$ K) calculated using Eqs. (34) and (35). These results are compared with experimental data for glass $x\text{Na}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ taken from Ref. 16. The values of parameters $\varepsilon_0 = 0.6$ eV, $\nu_0 = 3 \cdot 10^{13} \text{ s}^{-1}$, $l_0 = 3 \cdot 10^{-8} \text{ cm}$ were taken the same as the ones used above to fit the value of preexponential factor σ_0 in the expression for dc conductivity in the same glass $x\text{Na}_2\text{O} \cdot (1$

$-x$)B₂O₃. The value of coefficient β needed for the best fit of experimental data is 0.01. As has been already expected with respect to Eq. (29), the magnitude of β appears to be much less than unity. The first thing one should mention looking at curves in Fig. 4 is the difference in shape between experimental and theoretical curves. There could be two reasons for this difference: the assumed model can be not good enough to contain all the necessary physics, or the used theory is not precise enough, or, maybe, both of these reasons are responsible for the differences in the curve shapes between theory and experiment. Concerning the model, the roughest approximation in our view is the assumption that the potential relief does not depend on the concentration of mobile ions x . If one had information on such a dependence, one should definitely take it into account. We do not possess such information and therefore we took the simplest assumption that the potential does not depend on x . Concerning the theory, there are many order-of-magnitude estimates on the way from the initial formula (18) to the final results (34) and (35). Unfortunately, there is no better theory for $\sigma(\omega)$ in hopping systems that aims to describe a broad frequency range from $\omega=0$ to rather high frequencies ω . At least the scaling parameter provided by this theory agrees well with experimental data. A very slight divergence of the theoretical curves for different temperatures in Fig. 4 is caused by the above-mentioned rest temperature dependence of parameter $\Lambda_1 \propto (kT)^{\nu-\Delta+1} \cong (kT)^{-0.3}$. This divergence is, however, well within the accuracy of experimental results and it should not cause any trouble. Concluding, on comparison with experimental data in Fig. 4, one can mention that the cluster percolation theory developed by Zvyagin^{23,24} and applied to the random-energy model can account for the observed scaling behavior of the ratio $\sigma_{ac}(\omega, x, T)/\sigma_{dc}$, though improvements of the model and of the theory are desirable.

It is worth noting that an important aspect of the ionic conduction is left out of our scope in the above theoretical treatments. This is the influence of the long-range Coulomb interactions between carriers on the conducting properties. It is well-known that such interactions affect essentially hopping transport in various conditions (see, e.g., Ref. 19 and references therein). Moreover, these effects have already been considered for ionic hopping in glasses.⁸ It seems possible to account, e.g., for the nonlinearity of $\sigma_{dc}(x)$, by solely following the evolution of the long-range Coulomb potential with changing x . However, it is very unlikely that study of this potential can help to account for the mixed-alkali effect.

Therefore, we search in this report for the model that can account for the whole variety of puzzling effects known for ionic conduction in glasses. As shown above, the random-energy model subjected to the treatment within the percolation theory seems successful to account for such effects.

VI. CONCLUSIONS

The percolation approach is used to analyze dc and ac hopping conduction in ion-conducting glasses. It is shown that the most plausible model to account for experimental data is the random-energy model, according to which mobile ions contribute to conductivity by performing hops between

neighboring localized states in the glass matrix with rigid potential relief. This model is a natural extension of the random-barrier model used already for dc transport by Svare *et al.*¹¹ and by Sen *et al.*,¹² and for ac transport by Dyre.¹⁷ While the distribution of barriers is assumed in the random-barrier model, the random-energy model allows also the distribution of energies of localized states. This difference between the two models appears important, since the filling factors of localized states depend on their energies. The quantitative percolation approach within the random-energy model is formulated that accounts for most remarkable effects for ac and dc conductivity in ionic glasses. Among these effects are the mixed-cation effect, the strong nonlinearity of σ_{dc} in the single-modifier glasses with respect to the concentration of modifying ions and the scaling behavior of the ratio $\sigma_{ac}(\omega, x, T)/\sigma_{dc}$. It is worth noting that the random-energy model by Stevels¹³ and Taylor²⁵ in 1957, is, in fact, the earliest model suggested for ac and dc conduction of ionic glasses. One can argue that it is not very encouraging, especially for experimentalists, to have the end result of the theory in the form of a triple integral over unknown distributions [Eq. (51)]. However, this end result shows that the consequent application of the routine percolation arguments within the transport model existing since 1957 with choosing simplest possible distributions given by Eqs. (45) and (52) allows one to account not only qualitatively, but even quantitatively, for transport effects that are still considered as puzzling and challenging.¹ Therefore we believe that the rigorous percolation approach in the framework of the random-energy model provides a general basis for future study of transport phenomena in ion-conducting glasses.

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