

Bond Fluctuation Model of Superionic Conductors: Concepts and Applications

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Abstract

The bond fluctuation model of superionic conductors provides a framework to understand the characteristic properties of superionic materials. According to the model, the superionic behavior is related to a change of bonding that occurs locally and fluctuates in time. In the present report, after presenting the concept of the model and summarizing the main results obtained till now, some recent applications of the model is reviewed. Topics such as new interpretation of the power law exponent of ac conductivity observed in superionic glasses, model for the anomalous electronic properties observed in liquid silver chalcogenides, and prediction of nonlinear optical constants of ionic conducting glasses are covered.

Keywords: bond fluctuation model, superionic conductors, superionic glasses

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1. Introduction

Among the various classes of substances, there is a class of solid materials called superionic conductors. These materials are characterized by their high ionic conductivity with an order of magnitude as is usually found in molten salts. This high ionic conductivity is due to the movement of one kind of ion between sites provided by the immobile ion sublattice. Clarifying the mechanism of this exceptional high ionic conductivity has been a challenge for many decades. In the early studies, most of the approaches have been based on structural arguments [1, 2]. Structure is surely an important factor that determines the fast ion transport within the solid, but it is not the only factor. Recent studies have revealed that superionic conduction is closely related to the bonding characteristics of the materials [3-13].

Concerning the origin of superionic properties, the author has suggested that a change of bonding that occurs locally and fluctuates in time plays an important role [3-5]. There, it has been considered that local fluctuations of the bonding create a field of forces that move the ions, which in turn triggers new bond fluctuations. The mechanism of bond fluctuation in superionic conductors has been used successfully in the interpretation of various experimental observations [3, 14-17]. Theoretical studies based on a pseudopotential method also support the view that bond fluctuations may occur in superionic conductors [4, 5, 18, 19]. A simple phenomenological formulation of bond fluctuation in superionic conductors has been given by exploiting the analogies with the phenomenon of chemical equilibrium [20]. More recently, studies based on ab initio molecular dynamics simulations have confirmed the existence of bond fluctuation processes [21-24]. In the present paper, a brief review of the bond fluctuation model of superionic conductors is given. Early studies on the bond fluctuation model and other approaches related to the chemical bonding in superionic conductors have been already reviewed [25, 26, 11]. Therefore, in the present paper, only recent results obtained in the light of the bond fluctuation model are reviewed after introducing the concept and presenting the

main results of the model.

2. Bond Fluctuation Model

2.1 Empirical Background of the Model

The bond fluctuation model has an empirical background. By comparing the properties of a large number of compounds, it was found that a material behaves as superionic conductor if the following three criteria are met [3].

(a) The superionic conducting material must have an open structure. Within this structure, the mobile ion has a low coordination number. If the coordination number is equal, the mobile ion has a small ionic radius.

(b) The superionic conducting material shows a structural phase transition at relatively low pressure.

(c) For a material composed of atoms A and B, a parameter defined as $Z^* = (Z_A Z_B / \epsilon_0)^{1/2}$ exhibits a small value. Here, Z_A and Z_B are the valences and ϵ_0 is the static dielectric constant.

Specific values of material parameters related to the above criteria and discussions on the physical meaning of each criterion are given elsewhere [3, 25]. The important point that should be recognized is that a superionic conducting material fulfills all the three criteria. It should be mentioned that these criteria have much in common with the Phillips ionicity scale used widely in the literature [27]. It should be also mentioned that the above criteria have been obtained for relatively simple typical ionic conductors such as Ag and Cu halides and chalcogenides.

2.2 Concept of the Bond Fluctuation Model

Based on the empirical criteria described above, the following model of superionic conductors has been proposed [3, 4]. Consider a solid material in which the ions are vibrating around their lattice sites. As the position of the ion core moves, the electrons follow this movement and a deformation of the electronic cloud distribution takes place. On the other hand, the deformed electronic cloud creates new field of forces to move the ions. Within this picture of ion dynamics, the characteristic of superionic conductors resides in the fact that the electronic cloud deformation is induced easily. That is, a small disturbance in the electronic subsystem leads to a drastic change in the local structure of the ionic subsystem and vice versa. This idea has been described as a local fluctuation of the chemical bond which occurs within a superionic solid [3-5]. Fig. 1 illustrates schematically the concept of the model.

Phenomenologically, the net result of the microscopic bond fluctuation processes can be described as a double well potential [20]. It is gratifying to note that various theories of superionic conductors adopt this kind of potential [28-30]. By making connection with the structure, the fluctuation of the chemical bond is reflected in the coordination number of a diffusing ion at a particular instant. For instance, in the superionic conducting materials such as AgI and Cu halides, the mobile ion species Ag and Cu are surrounded by 4 anions in the low temperature non-superionic phase. In the superionic phase, the mobile ion takes instantaneously a different coordination number from 4 as it moves between sites provided by the cage ion sublattice. Many studies have revealed that among a wide variety of possible paths, an important path of the mobile ion is through the tetrahedral \rightarrow octahedral \rightarrow tetrahedral site occupation [31, 32]. That is, in the materials considered, an important type of local bond fluctuation that occurs accompanying the mobile ion dynamics is covalent \rightarrow ionic \rightarrow covalent bond fluctuations [3-5]. This prediction of the bond fluctuation model has been confirmed by ab initio molecular dynamics simulations.

2.3 Some Evidences of the Bond Fluctuation Processes

Experimental evidence for the fluctuations of the chemical bond has been investigated by measuring the temperature dependence of the dynamical effective charge [14, 15]. It has been shown that in the low temperature non-superionic phase, the effective charge decreases with the increase in temperature. On the other hand, in the high temperature superionic phase, the effective charge increases with temperature. It is known that the dynamical effective charges in typical semiconductors and ionic crystals decrease with the increase of temperature. Therefore, the temperature dependence of the effective charge in the superionic phase is anomalous. According to the bond fluctuation model, the anomaly is explained as due to the increase of ionic bonding configuration sites with the increase of temperature. Comparative studies of bonding performed in various materials support the conjectures given by the bond fluctuation model [4, 5, 18, 19].

As can be noted from the above discussions, to clarify the microscopic mechanism of superionic conduction, it is essential to consider the electronic state around the mobile ions as a function of time. This difficult task has been challenged and overcome by studying the dynamics of mobile ions in the superionic phase of some compounds by ab initio molecular dynamics simulations [21-24]. In the following, the main result obtained for CuI is shown.

The partial pair distribution functions $g_{\alpha\alpha}(r)$ are shown in Fig. 2. We can see that the average nearest neighbor distance of I-I pair is about 4.3 Å, which is much larger than that of Cu-I pair, which is about 2.6 Å. It must be noted that the average nearest neighbor distance of Cu-Cu pair is almost the same to that of Cu-I pair, in spite of the like ion correlation. This feature has also been found in the molten phase of CuI [33-35]. It seems that this anomalous short cation-cation distance is a characteristic of the structure of superionic conducting materials. It is worth to note that this feature does not appear in the pair distribution functions calculated by using the classical molecular dynamics simulations [36].

Figure 3 shows the total $D(E)$, and the partial $D_I(E)$, $D_{Cu}(E)$ electronic density of states. The origin of the energy is taken at the Fermi level ($E_F = 0$). In $D_I(E)$, the electronic states around -13 eV are s-like in character, and those between -7 and 0 eV are p-like. The large peak around -2 eV in $D_{Cu}(E)$ originates from 3d electronic states. It is evident that the 3d electronic states of Cu ions hybridize with the 5p state of ions with an energy range from -7 to 0 eV. This fact plays a fundamental role in the origin of bond fluctuation processes [3, 26].

In the superionic phase of CuI, the mobile Cu ions occupy two possible sites. Namely, the tetrahedral and octahedral sites in the fcc sublattice formed by the immobile I ions. Although the Cu ions prefer to occupy the tetrahedral sites, they must pass through an octahedral site when they migrate between two tetrahedral sites. Fig. 4 shows the isosurface of the electron density at 0.022 a.u. around a focused Cu ion when it is at the tetrahedral and octahedral sites. From Fig. 4 we can see clearly that when the Cu ion is in the tetrahedral site, the electron density distributes between the Cu ion and its neighboring I ions, so as to form covalent bonds. On the other hand, when the Cu ion is at the octahedral site, the electron density distributes spherically around Cu ions, suggesting an ionic bond.

To investigate the time evolution of bonding nature around the Cu ion, a population analysis has been performed by expanding the electronic wave functions in atomic orbital basis set [37]. The calculated time evolution of the gross charge shown in Fig. 5 indicates that the Cu ion pass from a tetrahedral cage to an octahedral cage at about $t = 0.6-0.7$ ps. Fig. 4(a) and Fig. 4(b) are snapshots of electron densities corresponding to $t = 0.3$ ps and $t = 1.5$ ps in Fig. 5, respectively. It is evident that the gross charge takes a large value when the Cu ion is in the octahedral site, while it takes a small value when it is in the tetrahedral site. The result confirms the predictions of the bond fluctuation model.

3. Recent Applications of the Bond Fluctuation Model

The concept of the bond fluctuations model has been applied widely to interpret many behaviors related to superionic transport. Among these, we can mention the temperature [14, 15] and pressure dependences [17] of the effective charge, estimation of the effective number of valence electrons [38], origin of the correlated motion between diffusing ions [3] or caterpillar mechanism [39], photoinduced ionic motion in chalcogenide glasses [16, 40, 41], and heat of transport due to collective motion of ions [42]. The bond fluctuation model was originally proposed to explain the properties of crystalline ionic conductors. However, it has found a fruitful field of application in disordered systems. This is not surprising, because the bond fluctuation model focuses its attention in the local dynamic atomic configuration and bonding. In the following, some recent applications are reviewed.

3.1 Role of the Medium Range Order of Glasses in the Ion Transport

Various structural studies in glasses have shown the presence of a characteristic peak at low values of momentum transfer [43]. This peak, which is called first sharp diffraction peak (FSDP), has been interpreted to arise from some kind of intermediate range ordering within the glass. There has been a lot of debate about the origin of FSDP. The specific interatomic correlations that originate the observed FSDP depend on the glass system under consideration.

The relationship between the ion transport properties and the FSDP wave number in some AgI containing oxide glasses has been studied [44, 45]. There, it has been found that the ionic conductivity increases and the activation energy decreases with the decrease of the FSDP wave number. Such a behavior has been explained by using the concept of bond fluctuations in superionic conductors. Glasses are prepared by cooling rapidly the melt before the system reaches its thermal equilibrium. Therefore, at the microscopic level, inhomogeneities of the

local structure and local chemical composition remain. A schematic energy barrier profile representing this situation is shown in Fig. 6. For instance, in AgI-AgPO₃ glasses, the network is formed by AgPO₃ and AgI is the doped salt. The distance that characterizes the medium range structure is denoted by d . The FSDP appears at $2\pi/d$.

If we focus on the Ag⁺ ions, we can distinguish at least three types of ions. The Ag⁺ ions in the doped salt which are bonded with I⁻, the Ag⁺ ions in the network which are bonded with O²⁻, and the Ag⁺ ions located in the boundary between network and doped salt which are bonded with I⁻ and O²⁻. According to the bond fluctuation model [3,4], the third type of Ag⁺ ions are more mobile than the others, because the Ag⁺ ion surrounded by different atoms feels an asymmetric field of forces which results in the anharmonic atomic vibration and large atomic migration. This situation is denoted in Fig. 6 as highly conducting regions and it is described by the average activation energy E_3 .

The relationship between the FSDP wave number and ion transport properties [44, 45] is understood by using the model represented in Fig. 6. By doping the network with salts, the characteristic distance d increases (decrease of the FSDP wave number). This is the network expansion reported by some authors [46]. By doping salt, the amount of highly conducting regions or the number of sites with low activation energies increase, which results in the increase of the ionic conductivity. Beside reproducing the observed FSDP – ion transport property relationship, the model predicts that the activation energy for ion transport initially decreases by doping salt, reaches a minimum at certain concentration, and increases by further doping, whereas in this course the FSDP wave number decreases monotonically [45]. It is gratifying to note that the evolution of the ionic conductivity predicted by the model has also been obtained by using percolation concepts in the analysis of composition dependence of diffusion in ion conducting glasses [47].

3.2 A New Interpretation for the Exponent of the Power Law of AC Conductivity

The above description concerned with DC conductivity. Recently, the relationship between the exponent of the power law behavior in the ac conductivity which is usually described as $\sigma(\omega) - \sigma(0) = A\omega^n + B\omega$, where A , B and n are constants, and the wave number of first sharp diffraction peak in some AgI containing oxide superionic glasses has been studied [48, 49]. There it was shown that the exponent of the power law increases with the decrease of the FSDP wave number. Concerning the origin of n , no consensus exists among the researchers [50, 51]. Some authors attribute it to some kind of interactions involving the mobile ions [52, 53]. Others connect it to some kind of geometric factors [54]. The correlation found between n and FSDP wave number suggests that the universal aspect of the power law discussed by many authors reflects the universal pattern of the potential barrier at intermediate length scales. This interpretation of n is new, not previously reported by any author. It must be mentioned however that some related works have been reported recently [55, 56]. For instance, the onset frequency of the ac conductivity in ion conducting glasses has been related to the fraction of high energy barriers that connect the clusters of fast ion conducting sites [55].

The correlation found between n and FSDP wave number can be understood as follows. Consider for instance the AgI-AgPO₃ glassy system. When the amount of doped salt AgI is small, most of the Ag⁺ ions arise from AgPO₃ that form the network which are bonded mainly to O²⁻ ions. Therefore, the highly conducting regions referred to in Fig. 6 do not extend over long distances. They are restricted in a limited region as indicated schematically by the spread regions around the network skeleton in Fig. 7(a). By increasing the amount of AgI, the number of Ag⁺ ions bonded to I⁻ and O²⁻ ions increases, which results in the increase of the highly conducting regions, or sites with low activation energies. At the same time, such sites connect to a large extent, which leads to an efficient ion transport over long distances. For this

case, note also that many channels for ion transport open, accompanying the increase of the highly conducting regions as illustrated in Fig. 7(b). The figure also shows the network expansion by salt doping which results in the decrease of the FSDP wave number [44, 46]. According to this model, the increase of the value of n is related to the increase of the number of channels available for ion transport. Such a result is in harmony with the finding of Sidebottom [54] that relates n to the dimensionality of ion transport pathways. The model which is illustrated in Fig. 6 predicts that the connectivity of the highly conducting regions will exhibit a maximum at certain values of salt doping [45]. Therefore, further salt doping over this particular concentration will result in the decrease of the connectivity of the highly conducting region as illustrated in Fig. 7(c). According to the relationship found, it is predicted that this situation will lead to the decrease of the exponent n .

3.3 Anomalous Electronic Properties of Liquid Silver Chalcogenides

The bond fluctuation model has also been used to interpret the anomalous electronic properties observed in liquid silver chalcogenides [57]. Among the various classes of liquid semiconductors, the systems Ag-S and Ag-Se exhibit unique electronic properties. It has been discovered that the electronic conductivity σ_e , of these systems shows a maximum at the stoichiometric composition Ag_2S and Ag_2Se [58, 59]. At the same composition, the temperature derivative of σ_e is also found to be negative. In contrast, other liquid semiconductors show a minimum in σ_e at the stoichiometric composition and the temperature derivative of σ_e is positive [60].

The origin of the anomalies has been investigated from a chemical bond point of view. The chemical trend in the charge transfer from one element to another within a condensed system can be obtained from the electronegativity difference between the elements of the system. The electronegativities of the elements as reported by Phillips [27] and the electronegativity

difference of Cu(Ag,Tl)-chalcogen is shown in Table 1. Among the systems tabulated, Ag-S and Ag-Se have larger differences in electronegativity. That is, the bonding in these two systems is more ionic than in others. This means that in Ag-S and Ag-Se the covalent to ionic bond fluctuation that occurs locally is induced more easily.

The electronic mobility in a condensed phase is intimately related with the interaction between atomic orbitals of the constituent atoms. If the overlap of orbitals is large, a large value of mobility will result. The idea is illustrated in Fig 8(a). Here, M and X represent Ag and chalcogen, respectively. A successful connection of X to another M will depend on the probability to find an atom M in the hatched region. In other words, the mobility of electronic carriers which is controlled by the percolation of interaction between second nearest neighbor orbitals [61], increases with the coordination number of M around M. In the cases of Ag₂S and Ag₂Se (compounds with large electronegativity difference), the bond fluctuation that persists in the liquid, results in a high Ag ion mobility and leads to a large probability to find a Ag ion in the hatched region. On the other hand, if the electronegativity difference is not so large as in Ag₂Te, the bond fluctuation is less frequent and the ionic mobility is decreased. This results in the decrease of probability to find a Ag ion in the hatched region when compared with Ag₂S and Ag₂Se. That is, in Ag₂Te (and other ordinary liquid semiconductors) the probability of path formation for the electronic carriers through the connection of orbitals is diminished when compared with Ag₂S and Ag₂Se. The situations discussed here are illustrated in Figs. 8(b) and 8(c). Neutron diffraction studies have found that the coordination number of Ag around Ag is about 10 in liquid Ag₂Se and 5.6 in liquid Ag₂Te [62], supporting the conjecture discussed. Fig. 9 shows the calculated behavior of the electronic conductivity in the presence and absence of bond fluctuation processes [57]. It is noted that the characteristic behavior found experimentally [58, 59] is reproduced.

3.4 Nonlinear Optical Constants

The most recent application of the bond fluctuation model concerns about nonlinear optical properties. The mechanism of ion transport through the bond fluctuation process suggests that ion conducting materials have high value of electronic polarizability. This prediction has been verified recently by comparing the magnitudes of the nonlinear optical constants of ionic conducting and other glasses. The comparison revealed that the nonlinear optical constants of superionic glasses are much larger than those of other glasses. Theoretical analysis based on bond orbital model applied to AgI containing borate glasses revealed that the origin of the enhancement in optical nonlinearity is related to the presence of d-electrons of Ag which plays also an important role in the ion transport processes [63]. The effect of the Ag d-electrons in the calculation of third order susceptibility is illustrated in Fig. 10. It shows clearly that by taking into account the Ag d-electrons, the agreement between the theoretical and the experimental values increases.

4. Conclusion

In this paper, the bond fluctuation model of superionic conductors has been briefly reviewed. It has been shown that the model provides a framework to understand many aspects related to the ion transport. According to the model, the superionic behavior is related to a change of bonding that occurs locally and fluctuates in time. It has been also shown that the concept of the model is applicable to a wide variety of materials that include crystalline materials, glasses and liquids. Till date, the application of the model has been limited to typical ionic conductors that contain Ag or Cu. It is expected that the concept of the bond fluctuation model could be applied to other ionic conductors. Further studies are required to step up the concept and to understand what factor is essential in the ion transport properties of solids.

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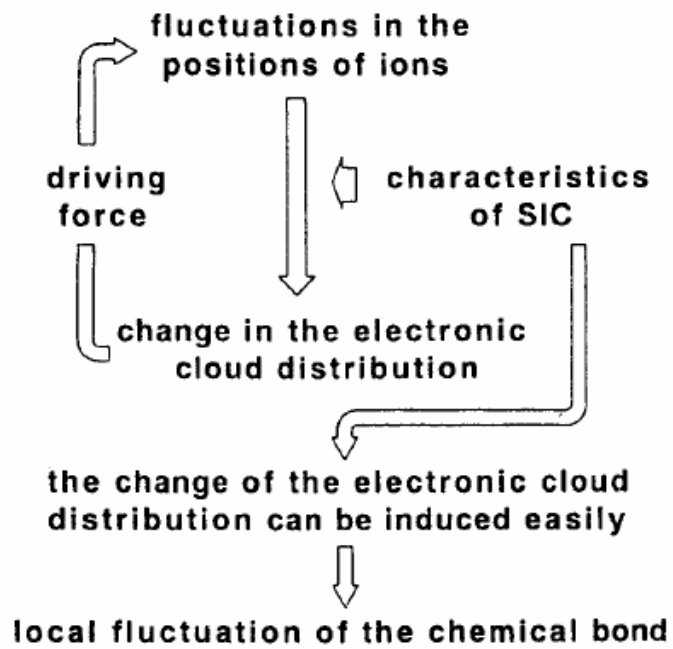


Fig.1. Schematic representation of the concept of bond fluctuation in superionic conductors.

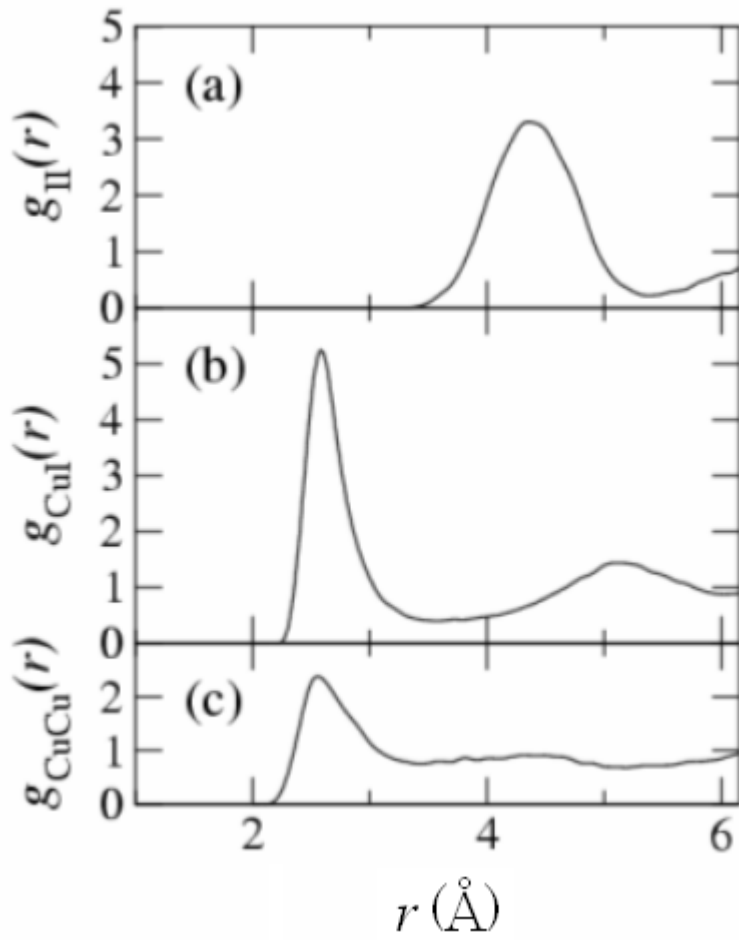


Fig.2. Partial pair distribution functions $g_{aa}(r)$ of (a) I-I, (b) Cu-I and (c) Cu-Cu in the superionic phase of CuI.

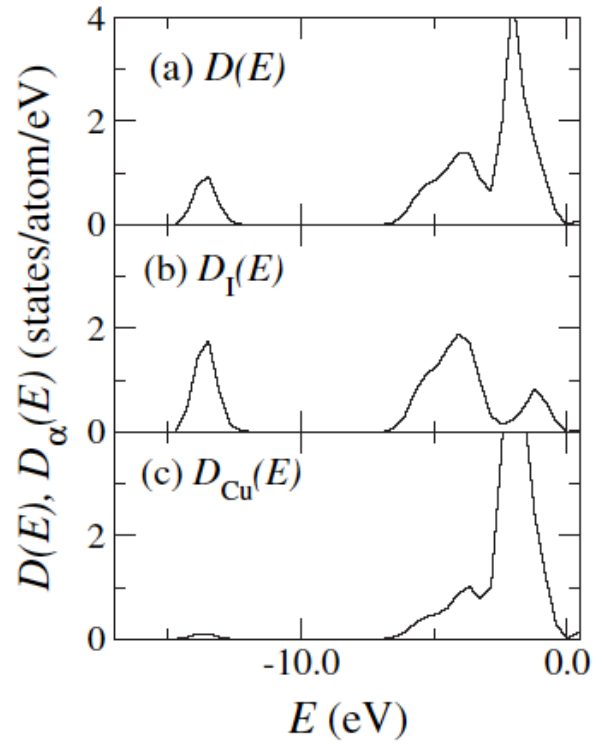


Fig. 3. Total electronic density of states $D(E)$ (a) and partial electronic densities of states $D_\alpha(E)$ for I (b) and Cu (c) ions in the superionic phase of CuI.

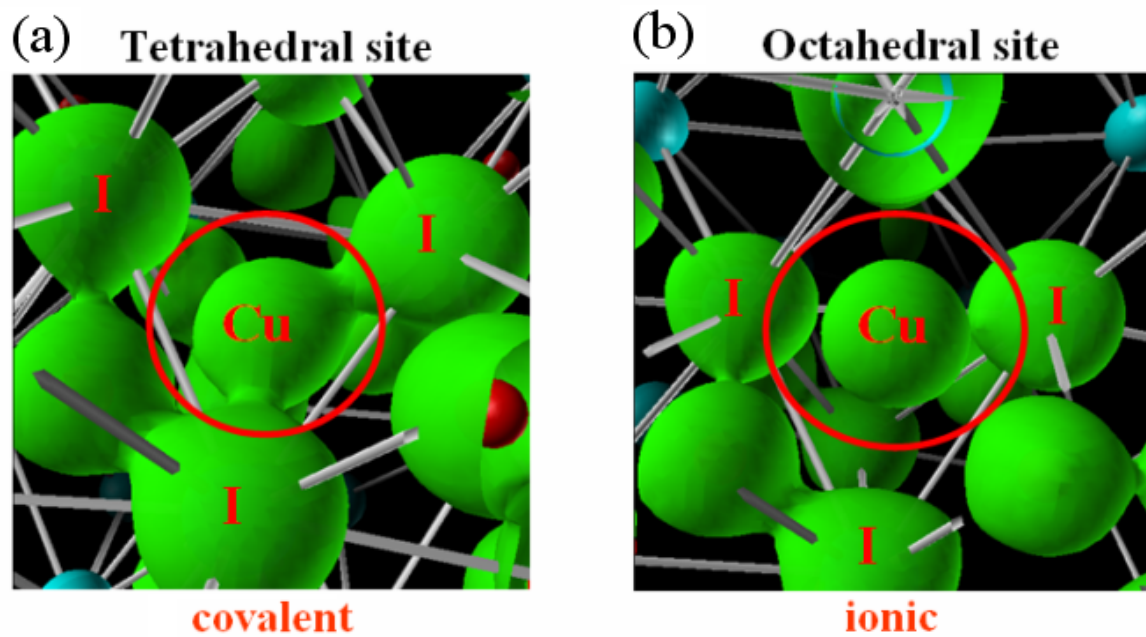


Fig. 4. Isosurface of electron density around the Cu ion at (a) the tetrahedral site and (b) octahedral site.

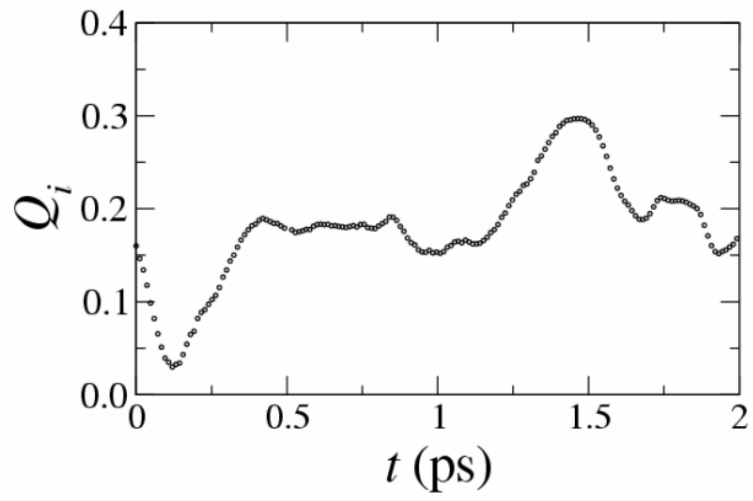


Fig. 5. Time evolution of the gross charge of Cu ion in CuI. The vertical axis scale is defined as the difference from the nominal number of valence electrons.

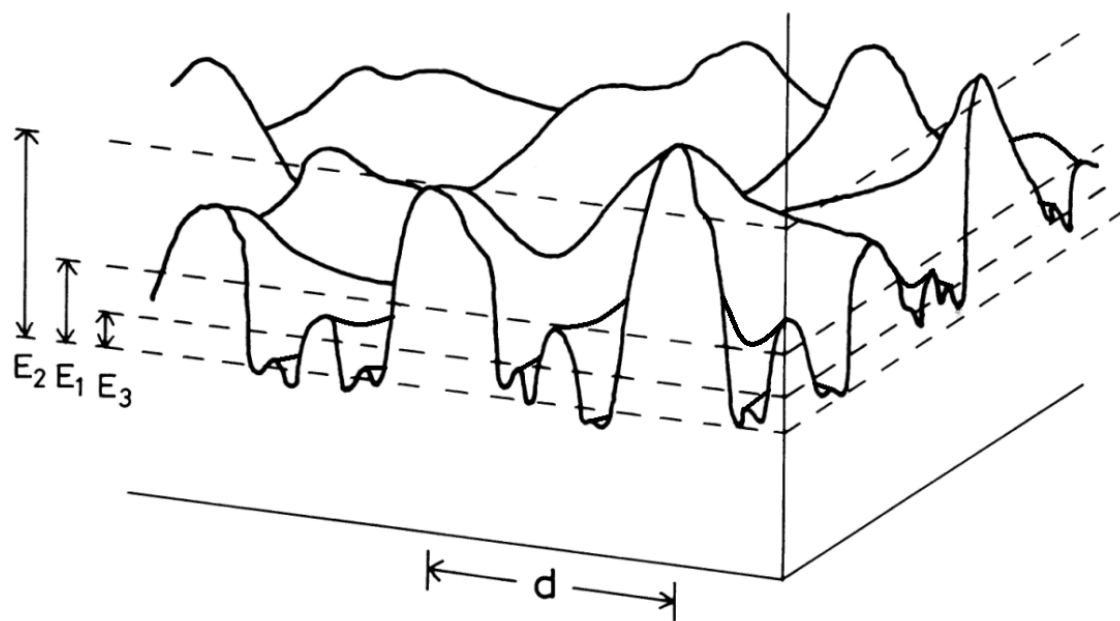


Fig. 6. A schematic representation of the energy barrier profile in superionic glasses. E_1 and E_2 are the average values of the activation energies in the doped salt and in the network, respectively. E_3 is the activation energy of the highly conducting region. d is a characteristic distance that defines the medium range structure.

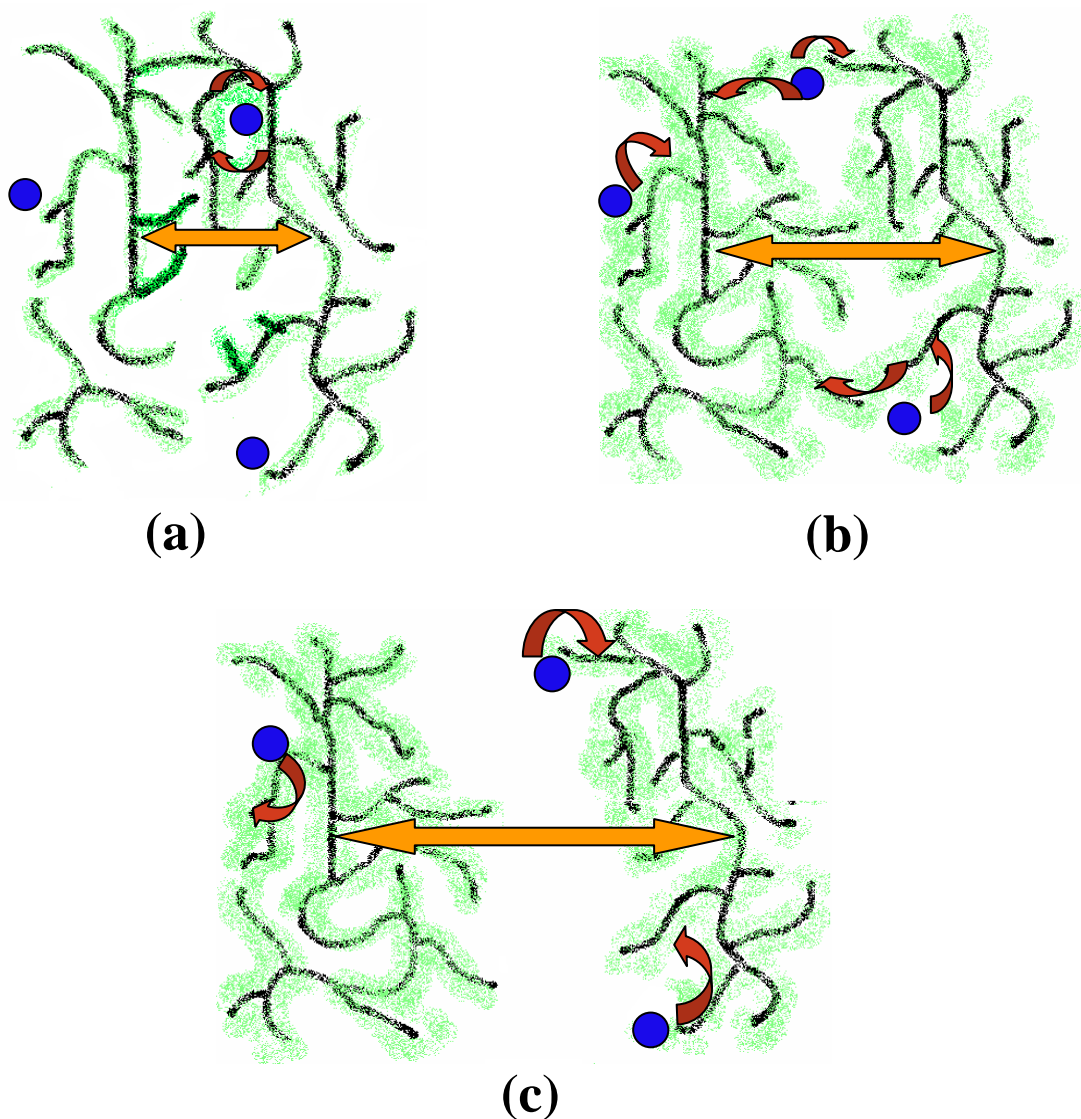


Fig. 7. A schematic representation showing how the connectivity of the highly conducting regions, or the low activation energy sites (illustrated as spreads around the network skeleton) vary with the concentration of doped salts (not explicitly shown for clearness). The doped salt concentration increases from (a) to (c) and expands the network separation.

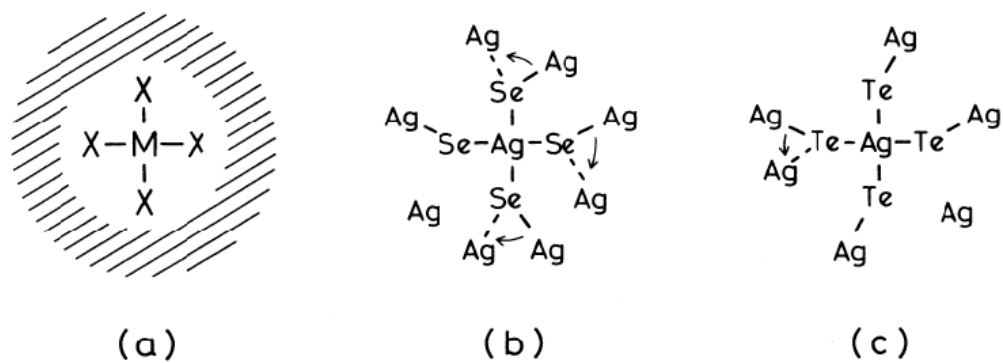


Fig. 8. (a) The connection of X to another M depends on the probability to find M in the hatched region. (b) The bond fluctuation leads to an increase of the coordination number of Ag around Ag. (c) The strong covalency is unfavorable for the bond fluctuations.

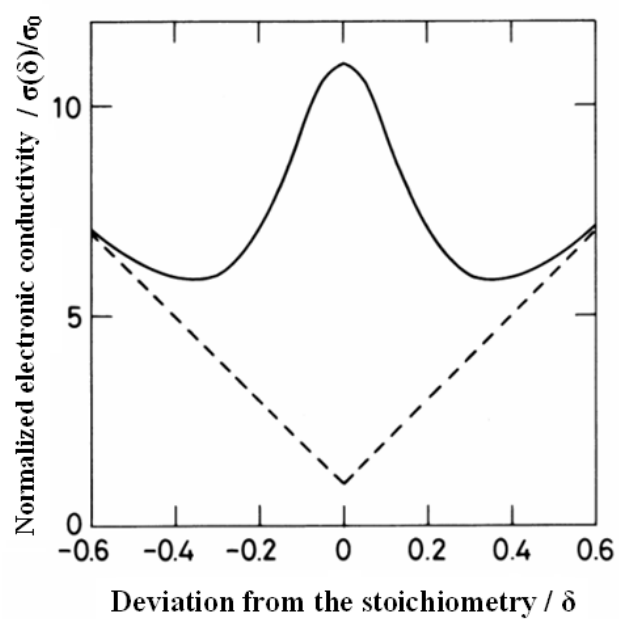


Fig. 9. Schematic representation of the behavior of electronic conductivity in the presence (solid line) and absence (broken line) of bond fluctuation processes.

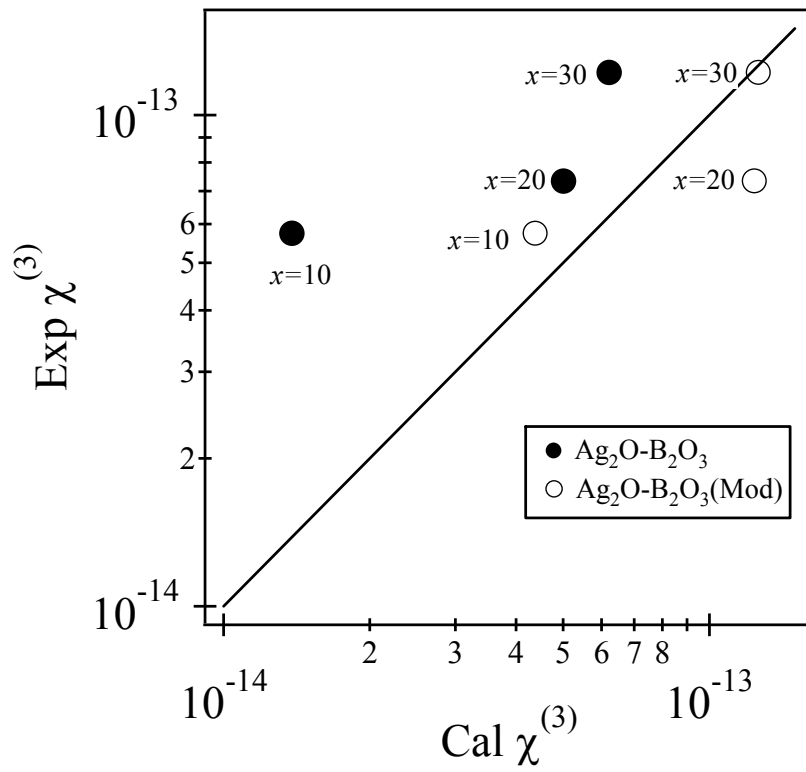


Fig. 10. Calculated and measured values of the third order nonlinear optical constants for $x\text{Ag}_2\text{O}-(100-x)\text{B}_2\text{O}_3$ glasses. The effects of the d-electrons in the calculated values are shown by full and open circles. Open circles take into account the d-electrons of Ag.

Table 1. Electronegativity values [27] and the electronegativity differences.

Electronegativity	$\Delta \chi = \chi_{\text{anion}} - \chi_{\text{cation}}$
$\chi_{\text{Cu}} = 0.79$	$\Delta \chi_{\text{Cu-S}} = 1.08$
$\chi_{\text{Ag}} = 0.57$	$\Delta \chi_{\text{Cu-Se}} = 1.00$
$\chi_{\text{Tl}} = 0.94$	$\Delta \chi_{\text{Cu-Te}} = 0.68$
$\chi_{\text{S}} = 1.87$	$\Delta \chi_{\text{Ag-S}} = 1.30$
$\chi_{\text{Se}} = 1.79$	$\Delta \chi_{\text{Ag-Se}} = 1.22$
$\chi_{\text{Te}} = 1.47$	$\Delta \chi_{\text{Ag-Te}} = 0.90$
	$\Delta \chi_{\text{Tl-S}} = 0.93$
	$\Delta \chi_{\text{Tl-Se}} = 0.85$
	$\Delta \chi_{\text{Tl-Te}} = 0.53$