

A MODEL FOR THE ANOMALOUS ELECTRONIC PROPERTIES IN LIQUID SILVER CHALCOGENIDES: IMPLICATIONS FROM A VISCOELASTIC THEORY

Masaru Aniya*

Department of Physics, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

Abstract

The electronic conductivity in liquids Ag-S and Ag-Se systems exhibits a maximum and a negative temperature derivative at the stoichiometric composition Ag_2S and Ag_2Se . In a similar alloy, Cu-chalcogenides and other liquid semiconductors, such anomalies have not been observed. In the present paper, a model that explains the origin of the anomaly is presented. It is suggested that the anomalous behavior is controlled by the connection between the second nearest neighbor orbitals. Such connection depends on the electronegativity difference between the constituent elements of the system and is intimately related with the superionic behavior that these materials exhibit in the solid phase.

Keywords: *bond fluctuation model, electronic properties, liquid semiconductors, silver chalcogenides, superionic conductors*

Introduction

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 [1,2]. At the same composition, the temperature derivative of σ_e is also found to be negative [1,2]. In contrast, other liquid semiconducting alloys show a minimum in σ_e at the stoichiometric composition and the temperature derivative of σ_e is positive [3]. In order to understand the origin of these unusual behavior, various properties have been measured [1,2,4,5,6]. Theoretical studies concerning the electronic structure of liquid silver chalcogenides have been also published [7,8]. However, the mystery remains unsolved.

It is well known that silver chalcogenides and related copper chalcogenide compounds transform to the so-called superionic conducting phase before melting [9]. The superionic phase is characterized by its high ionic conductivity, with an order of magnitude as is usually found in

molten salts. There, the large ionic conductivity is due to the movement of one part of ions between sites in the immobile ion structure. In the case of silver (copper) chalcogenides, the mobile species are Ag(Cu). Concerning the origin of superionic transport, the author has suggested that a change of bonding which occurs locally and fluctuates in time is playing an important role [10,11]. By considering such bond fluctuation processes, satisfactory explanation has been given for many properties observed in superionic conductors [10-14]. Pseudopotential studies of bonding [11,14] and *ab initio* molecular dynamics studies [15,16] support the existence of such bond fluctuation processes in superionic conductors.

The aim of the present paper is to investigate if the unusual electronic properties observed in liquids Ag₂S and Ag₂Se are related to the superionic properties of these compounds. By reinterpreting the reported data up to now in the light of bond fluctuation processes mentioned above, it will be shown that such is the case.

Composition dependence of the ionic conductivity and the viscoelastic theory

Before discussing how it is possible to give an explanation to the unusual electronic properties observed in liquids Ag₂S and Ag₂Se, it will be convenient to look the composition dependence of the ionic conductivity. Based on the observations that superionic conductors such as silver chalcogenides exhibit an intermediate behavior between solids and liquids, the interpenetrating two fluid model for the superionic melt has been proposed [17]. This viscoelastic model has been applied successfully to describe the composition dependence of sound velocity [17], collective modes [18], atomic transport properties in binary [19] and ternary [20] systems. One relevant prediction from such a model that is related with the present study is the composition dependence of the diffusion coefficient in liquid Ag-Se system [19]. As shown in Fig. 1, the model predicts that the diffusion coefficient will exhibit a maximum at the stoichiometric composition Ag₂Se. This prediction is consistent with the measured behavior of the composition dependence of the ionic conductivity in liquid Ag-Se shown in the inset [21]. It should be noted that the peak at the stoichiometric composition appears when the Thomas-Fermi screening wave number K_{TF} or the electronic number concentration is decreased. This behavior provides a useful insight in the construction of the model presented in this paper as will be shown later.

Mechanism of superionic transport and the electronegativity difference

According to the bond fluctuation model of superionic conductors mentioned in the Introduction, in compounds such as AgI, Cu halides, Ag and Cu chalcogenides, the high ionic mobility results

when the ionic bonded sites emerge as a fluctuation in the covalent bonded matrix. That is, the mobile ion dynamics is accompanied by the change of the electronic cloud distribution. Since the site where the change of bonding occurs is unstable, its propagation triggers new bond fluctuating sites, which result in the correlated ion movements [10,11]. This kind of ion dynamics has been firmly confirmed by *ab initio* molecular dynamics studies [15]. In Fig. 2, a snapshot of the atomic dynamics in CuI is shown when the Cu atom is in the tetrahedral site and in an octahedral site. Measurements of the temperature dependence of the dynamical effective charge in AgI and Ag₃SI [12] have indicated that the ionicity of the compound increases in the superionic phase. Comparative studies of bonding in various compounds by using a pseudopotential method, also support the view that ionic bonded sites are induced easily in superionic compounds such as AgI and Cu halides than in non-superionic compounds such as GaAs, InSb, ZnSe, etc. [11,14]. The mechanism of ion transport suggested by the bond fluctuation model [10,11,14] is also in agreement with the result of a recent study that suggests the importance of structural flexibility in the ion transport processes [22].

The chemical trend in the charge transfer from one atom 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 [23] and the electronegativity difference of Cu(Ag,Tl)-chalcogen are shown in Table 1. The system Tl-chalcogenides is included here for comparison. The liquid Tl-chalcogenides shows behavior typical of liquid semiconductors in their electronic properties [3].

Among the systems tabulated in Table 1, Ag-S and Ag-Se have large differences in electronegativity. That is, the bonding in these two systems are more ionic than the others. This means that in Ag-S and Ag-Se the covalent to ionic bond fluctuation that occurs locally is induced more easily. An immediate consequence of this induction is that the ionic conductivity will decrease as the electronegativity difference decreases due to a decrease in the magnitude of bond fluctuations. The pertinence of this statement is verified experimentally in the solid phase [24]. In the liquid phase, the same conclusion is expected to apply, because the chemical trend is not expected to differ from that of the solid state. Moreover, if a system has a strong tendency to be a superionic conductor, it will show a strong tendency to sublattice ordering even in the liquid phase [25], and consequently, the temperature derivative of the ionic conductivity might be positive as in the superionic phase. On the other hand, if a system has a weak tendency to be a superionic conductor, the bond fluctuation is less effective in moving the ions, and consequently, the ionic conductivity in the liquid phase will decrease with the increase of temperature. Among the materials given in Table 1, Ag-S and Ag-Se are the systems which show strong tendencies to become superionic conductors, because their large electronegativity difference favors bond fluctuations. Experimental study on ionic conductivity in the liquid phase has revealed that $\sigma_i(\text{Ag}_2\text{S}) > \sigma_i(\text{Ag}_2\text{Se}) > \sigma_i(\text{Ag}_2\text{Te})$ and that $d\sigma_i(\text{Ag}_2\text{S}) / dT > 0$, $d\sigma_i(\text{Ag}_2\text{Se}) / dT > 0$,

$d\sigma_i(\text{Ag}_2\text{Te})/dT < 0$ [26]. These behaviors are consistent with the discussions given above.

To avoid misunderstanding, a comment is given here. The statement that large electronegativity difference favors bond fluctuation and leads to superionic behavior is valid for four-fold coordinated compounds such as Ag(Cu) chalcogenides. It does not apply for instance to NaCl, which has a larger electronegativity difference than silver chalcogenides, but is a six-fold coordinated compound [10,11,14]. Moreover, in the solid phase, such four-fold coordinated compounds must show a structural instability under the action of relatively small external pressure (less than ~ 30 kbar) [10].

Model for the anomalous electronic properties

A schematic view of the evolution of energy diagram in a metal- chalcogenide system is illustrated in Fig. 3 for the case of Ag-Se system. As Se is introduced into the Ag matrix, the formation of covalent Ag-Se bonds takes place, and near the stoichiometric composition, the energy diagram as illustrated in Fig. 3 is formed. Note that near the stoichiometric composition, the energy diagram is similar to that of doped semiconductors [27]. Since $\text{Ag}_{2+\delta}$ and $\text{Ag}_{2-\delta}$ behave as *n*- and *p*-type semiconductors respectively, a *n-p* transition is expected to occur near the stoichiometric composition Ag_2Se . Indeed, experimentally, the thermoelectric power in liquid $\text{Ag}_{1-x}\text{Se}_x$ is found to change sign from negative to positive around the stoichiometric composition [2].

The electronic conductivity is given by $\sigma_e = ne\mu$, where *n* is the number density of carriers, *e* is the electronic charge and μ is the mobility. Based on this expression, the maximum of σ_e observed in liquids Ag_2S and Ag_2Se is traced back to the increased value of the mobility at the stoichiometric composition. The alternative possibility, that is, the increase of *n* seems unphysical, because at the stoichiometric composition the chemical stability due to charge transfer within the compound is maximized and the number of carriers decreases.

The problem is why the mobility in liquids Ag-S and Ag-Se increases at the stoichiometric composition. The mobility is given by $\mu = e\tau/m$, where τ is the relaxation time and *m* is the effective mass of the carriers [27]. The 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, the effective mass will be small and it will give a large value of mobility.

Studies based on the bond orbital model have revealed that the curvature of the valence band is governed by the interaction between second nearest neighbor orbitals [28]. Since the effective mass is intimately related with the curvature of the band, the mobility of carriers is controlled by the interaction of such orbitals. In order to see more clearly this effect, an example is shown in Fig. 4 for the case of antifluorite structure. This structure resembles the structures of β - Ag_2S , α - Ag_2Te , α - Cu_2S , and α - Cu_2Se in the superionic phases [9]. In Fig. 4, the bonding orbitals

and their interactions up to second nearest neighbor are also shown. Here M and X represent the metal and chalcogen atoms, respectively. The metal is surrounded by four chalcogens [4,9], while the chalcogen is assumed to bind with two metal atoms based on valence arguments. In the notations of Fig. 4, the interactions V_s and V_d control the mobility.

Strictly speaking, the above discussion is valid for a crystal in the solid state. However, since the short range structure of liquids and solids is similar, the above picture can be applied also to liquids. In the liquid phase, due to a large thermal disturbance, the connection of the orbitals to those of the second, third, ...nearest neighbor atoms is diminished. That is, as far as the second nearest neighbor is concerned, the magnitudes of the interaction parameters V_s and V_d decrease with temperature. It is at this point that the peculiarity of Ag_2S and Ag_2Se enters. In order to make the comprehension easy, consider the Fig. 5(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, increases with the coordination number of M around M. In the cases of Ag_2S and Ag_2Se (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 Ag_2Te , the bond fluctuation is less frequent and the ionic mobility decreases. This results in the decrease of probability to find a Ag ion in the hatched region when compared with Ag_2S and Ag_2Se . That is in Ag_2Te (and other ordinary liquid semiconductors), the probability of path formation for the electronic carriers through the connection of orbitals is diminished when compared with Ag_2S and Ag_2Se . Related to this view it can be said that in the case of Ag_2Te , the strong directed bond which results from its covalency decreases the probability of finding an Ag ion in the hatched region. The situations discussed here are illustrated schematically in Figs. 5(b) and 5(c). Neutron diffraction measurements have found that the coordination number of Ag around Ag is about 10 in liquid Ag_2Se and 5.6 in liquid Ag_2Te [4]. These experimental results support the conjecture given above. From the above discussions it is now clear, why the electronic carrier mobility in liquids Ag_2S and Ag_2Se increases, while in liquid Ag_2Te such effect is not observed [29]. It should be mentioned however, that recent measurement in liquid Ag-Te system has detected an anomalous peaked behavior in the electronic conductivity similar to those observed in Ag-S and Ag-Se [30]. However, its magnitude is much smaller compared with those observed in Ag-S and Ag-Se, and the anomalous negative temperature dependence of the electronic conductivity near the stoichiometric composition is not observed. Therefore, the discussions given above remain valid.

Concerning the coordination number of Ag around Ag mentioned above, it is quite probable that the large number found in Ag_2Se is related with the inhomogeneous Ag distribution. For the case of liquid CuI, it has been shown clearly by *ab initio* molecular dynamics studies that the

distribution of Cu is inhomogeneous [31]. Reflecting this inhomogeneity, the first peak of the partial pair distribution of Cu-Cu and Cu-I appears at almost the same distance [31]. Similar structural characteristics have been also found in liquid AgI [32] and liquid Ag₂Se [16]. This finding could be incorporated into the model of this paper, whose essence is represented schematically in Fig. 5(a), by considering the M-M bonds in addition to M-X-M bonds.

Near the stoichiometric composition, the conductivity is given by

$$\sigma(\delta, T) = en(\delta, T)\mu(\delta, T), \quad (1)$$

where T is the temperature and δ is the deviation from the stoichiometric composition. By noting that near the stoichiometric composition the system can be considered as doped semiconductors, the number density of carriers is written as

$$n = n_0 + N_0|\delta|, \quad (2)$$

where n_0 is the carrier number density at the stoichiometric composition and N_0 is the number of M ions per formula unit and per volume unit. The mobility of the carriers depends on the degree of percolation of the interaction between second nearest neighbor orbitals as discussed above. Moreover, such degree of percolation is maximized at the stoichiometric composition, because at such composition the chemical stability of the system is maxima. That is, the length of the connection of the type ...-M-X-M-X-M-... is maximum at the stoichiometric composition. Of course, such connection is fluctuating in space and in time. This observation leads us to write the following expression for the mobility in analogy with an expression of the theory of correlation functions [33].

$$\mu = \mu_0 \left[1 + \lambda' \frac{\exp(-R'/\xi)}{R'} \right], \quad (3)$$

where μ_0 is the value of the mobility at the stoichiometric composition and in the absence of bond fluctuation processes. λ' is a material parameter that depends on the electronegativity difference of the constituents and gives the magnitude of bond fluctuations. It depends also on temperature as will be described later. The factor $\exp(-R'/\xi)/R'$ describes the spatial extent of the connection of orbitals mentioned above and R' is the distance. ξ is the correlation length.

The electronic carriers which result from the deviation from the stoichiometry, screen the interactions between the ions. That is, the strength of the -M-X-M- connection diminishes with the deviation from the stoichiometry. In previous section it was shown that the viscoelastic theory

predicts a peaked behavior in the diffusion coefficient and that this behavior is confirmed experimentally by the measurement of ionic conductivity. It was also shown that the peaked behavior depends on the Thomas-Fermi screening wave number or the electronic carrier number density. The microscopic origin of such a behavior is traced back to the strength of the connectivity of -M-X-M-. The strong connectivity originates the correlated ion motion (mediated by the local electronic cloud distribution change), which results in the enhanced high ionic conductivity. Based on the above considerations, the correlation length is written as

$$\xi = C' / |\delta|, \quad (4)$$

where C' is a constant. Then, Eq. (3) is rewritten as

$$\mu = \mu_0 [1 + \lambda \exp(-C|\delta|)], \quad (5)$$

where $\lambda = \lambda' / R'$ and $C = R' / C'$. Inserting Eqs. (2) and (5) into Eq. (1) we have

$$\sigma = \sigma_0 [1 + (N_0 / n_0) |\delta|] [1 + \lambda \exp(-C|\delta|)], \quad (6)$$

where $\sigma_0 = en_0\mu_0$.

In the absence of bond fluctuation processes, or when these processes can be neglected (as in ordinary liquid semiconducting systems) we have by putting $\lambda = 0$,

$$\sigma = \sigma_0 [1 + (N_0 / n_0) |\delta|]. \quad (7)$$

The behaviors of Eqs. (6) and (7) is shown schematically in Fig. 6. Note that although qualitatively, the mysterious behavior found experimentally [1,2] is reproduced.

The temperature dependence of the electronic conductivity can be understood as follows. Since we are viewing the systems M_2X and $M_{2+\delta}(M_{2-\delta})$ as intrinsic and doped semiconductors respectively, the number density of carriers can be written as [27]

$$n_0 = A \exp(-E_g / k_B T),$$

$$N_0|\delta| = B|\delta|^{1/2} \exp(-E_i / 2k_B T), \quad (8)$$

where A and B are constants, E_g is the energy gap of M_2X and E_i is the energy level of the impurity in the matrix M_2X . Eq. (8) indicates that the number density of carriers increases with temperature due to thermal excitations. On the other hand, as the temperature increases, the connection between second nearest neighbor orbitals diminishes due to thermal disturbance. In terms of the interaction parameters of Fig. 4, the number of bonds described by V_s and V_d decreases with temperature. Therefore, the electronic mobility decreases with temperature. The decrease of the connection leads to the decrease in the efficiency of bond fluctuation processes. Such an effect of the temperature is described as

$$\lambda = \lambda_0 \exp(-\alpha T). \quad (9)$$

Here, λ_0 is a material parameter that depends purely on the electronegativity difference of the constituents and α is a constant. μ_0 depends also on temperature. For instance, in the solid state, if the dominant electron scattering mechanism is due to phonons, we have $\mu \propto T^{-3/2}$ [27]. Here it is assumed that

$$\mu_0 = GT^{-t}, \quad (10)$$

where G is a constant and t is a number of order unity.

Inserting Eqs. (8), (9) and (10) into Eq. (6) we obtain

$$\begin{aligned} \sigma = eGT^{-t} [A \exp(-E_g / k_B T) + B|\delta|^{1/2} \exp(-E_i / 2k_B T)] \\ \cdot [1 + \lambda_0 \exp(-\alpha T) \exp(-C|\delta|)]. \end{aligned} \quad (11)$$

For large $|\delta|$, we have $\mu \approx \mu_0$, $n \approx N_0|\delta|$ and

$$\sigma = eBGT^{-t} |\delta|^{1/2} \exp(-E_i / 2k_B T). \quad (12)$$

Since the exponential function dominates, the conductivity increases with the increase of temperature. That is, for large deviation from the stoichiometry, the temperature dependence of the conductivity is controlled by the thermal excitations of the carriers. This is the behavior found in ordinary semiconductors [3] and in liquids Ag-S and Ag-Se outside the stoichiometric compositions [1,2] (for instance at $\text{Ag}_{70}\text{Se}_{30}$ and $\text{Ag}_{60}\text{Se}_{40}$). On the other hand, at the stoichiometric composition we have

$$\sigma = eAGT^{-t} \exp(-E_g / k_B T)[1 + \lambda_0 \exp(-\alpha T)]. \quad (13)$$

In the absence of bond fluctuations or when these processes can be neglected, the above equation reduces to

$$\sigma = eAGT^{-t} \exp(-E_g / k_B T). \quad (14)$$

Eq. (14) describes the behavior of Ag_2Te [29], Cu_2X ($\text{X} = \text{S}, \text{Se}, \text{Te}$) [34] and other liquid semiconductors that show usual behavior in the composition dependence of the electronic conductivity. If the bond fluctuation is present, the term $\lambda_0 \exp(-\alpha T)$ survives, and originates the negative temperature derivative of the electronic conductivity observed in liquids Ag_2S and Ag_2Se [1,2].

In this section, a model for the anomalous electronic properties found in the composition and temperature dependencies of liquids Ag-S and Ag-Se has been presented. We have shown how the different materials properties reported till now can be correlated harmonically. As far as the author is informed, this is the first model that explains the anomalous behavior. Thermal analyses have been performed to study the effect of additives in some chalcogenide systems [35,36]. Concerning the system in consideration, no detailed thermal study has been performed yet. Thermal studies are recommended to gain further insight into the properties of liquid silver chalcogenides.

Conclusion

In the present paper, the origin of the anomalous electronic properties observed in liquids Ag-S and Ag-Se has been investigated. It is suggested that the anomalous behavior are controlled by the connection of the second nearest neighbor orbitals. Such connection depends on the electronegativity difference between the constituent elements of the system and is intimately related to the superionic behavior that these compounds exhibit in the solid phase. According to

the bond fluctuation model of superionic conductors proposed by the author, the local change of the chemical bond plays a fundamental role to originate the correlated ion dynamics. In the liquid phase such fluctuations persist, which lead from time to time to the formation of the connection of the bonds between the second nearest neighbors mentioned above. The model presented in the present paper provides also an understanding of diverse material properties such as temperature dependence of the electronic and ionic conductivities, *p-n* transition observed in the thermopower measurement and structural characteristics. It has been also shown that the predicted behavior of the composition dependence of the diffusion coefficient by a viscoelastic theory is in harmony with the model presented in this paper and with the experimental result of composition dependence of ionic conductivity.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Area (439) from the Ministry of Education, Culture, Sports, Science and Technology of Japan and by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (No. 19560014).

References

1. Ohno S, Barnes AC, Enderby JE. The electrical conductivity and thermopower of liquid $\text{Ag}_{1-x}\text{S}_x$ alloys near the stoichiometric composition Ag_2S . *J Phys Condens Matter*. 1990;2:7707-14.
2. Ohno S, Barnes AC, Enderby JE. The electronic properties of liquid $\text{Ag}_{1-x}\text{Se}_x$. *J Phys Condens Matter*. 1994;6:5335-50.
3. Enderby JE, Barnes AC. Liquid semiconductors. *Rep Prog Phys*. 1990;53:85-179.
4. Price DL, Saboungi ML, Susman S, Volin KJ, Enderby JE, Barnes AC. Structure of two liquid semiconductors $\text{Ag}_{1-x}\text{Se}_x$ and $\text{Ag}_{0.67}\text{Te}_{0.33}$. *J Phys Condens Matter*. 1993;5:3087-94.
5. Usuki T, Itoh K, Uemura O, Kameda Y. Semiconducting behavior in the liquid $\text{Ag-Ag}_2\text{X}_3$ system (X:Te, Se). *Ber Bunsenges Phys Chem*. 1998;102:656-62.
6. Hamilton MA, Barnes AC, Howells WS, Fischer HE. Ag^+ dynamics in the superionic and liquid phases of Ag_2Se and Ag_2Te by coherent quasi-elastic neutron scattering. *J Phys Condens Matter*. 2001; 13:2425-36.
7. Kirchhoff F, Holender JM, Gillan MJ. Structure, dynamics, and electronic structure of liquid Ag-Se alloys investigated by ab initio simulation. *Phys Rev B*. 1996;54:190-202.

8. Koslowski T. The electronic structure of liquid silver chalcogenides: a tight-binding approach. *J Phys Condens Matter*. 1996;8:7031-9.
9. Chandra S. Superionic solids. Amsterdam, North-Holland; 1981.
10. Aniya M. A chemical approach for the microscopic mechanism of fast ion transport in solids. *Solid State Ionics*. 1992;50:125-9.
11. Aniya M. Pseudopotential study of bonding in the superionic material AgI. *J Phys Soc Jpn*. 1992; 61:4474-83.
12. Aniya M, Wakamura K. Temperature dependence of the dynamical effective charge in Ag₃SI. *Solid State Ionics*. 1996;86-88:183-6.
13. Aniya M. A model for the photo-electro ionic phenomena in chalcogenide glasses. *J Non-Cryst Solids*. 1996;198-200:762-5.
14. Aniya M. The bond fluctuation model of superionic conductors: a review. *Rec Res Develop Phys Chem Solids*. 2002;1:99-120.
15. Shimojo F, Aniya M. Diffusion of mobile ions and bond fluctuations in superionic conductor CuI from ab initio molecular-dynamics simulations. *J Phys Soc Jpn*. 2003;72:2702-5.
16. Shimojo F, Aniya M. Diffusion mechanism of Ag ions in superionic conductor Ag₂Se from ab initio molecular-dynamics simulations. *J Phys Soc Jpn*. 2005;74:1224-30.
17. Aniya M, Iseki T. A model for the composition dependence of sound velocity in liquid silver chalcogenides. *J Non-Cryst Solids*. 2002;312-314:400-3.
18. Ogawa H, Kobayashi M, Iseki T, Aniya M. Collective motion in liquid silver chalcogenides. *J Phys Soc Jpn*. 2005;74:2265-9.
19. Aniya M, Shimojo F, Iseki T. Composition dependence of diffusion in liquid silver chalcogenides. *J Non-Cryst Solids*. 2004;338-340:579-81.
20. Ikeda M, Aniya M. A hydrodynamic model for the collective motion in Ag-Cu-Se. *Solid State Ionics*. 2008;179:761-4.
21. Usuki T, Abe K, Uemura O, Kameda Y. Ionic conduction in liquid Ag-Se and Ag-Te systems. *J Phys Soc Jpn*. 2001;70:2061-7.
22. Mohn CE, Stølen S. Average and local structure of α -CuI by configurational averaging. *J Phys Condens Matter* 2007;19:466208.
23. Phillips JC. Bonds and bands in semiconductors. New York: Academic Press; 1973.
24. Miyatani S. Ionic conductivity in silver chalcogenides. *J Phys Soc Jpn*. 1981;50:3415-8.
25. Aniya M, Okazaki H, Kobayashi M. Static dielectric function of superionic conductor α -AgI. *Phys Rev Lett*. 1990;65:1474-7.
26. Endo H, Yao M, Ishida K. Ionic conductivity and electronic properties of liquid Ag chalcogenides up to 1500 °C. *J Phys Soc Jpn*. 1980;48:235-7.
27. Kawamura H. Handoutai butsuri. Tokyo: Kyoritsu; 1987.
28. Harrison WA. Electronic structure and the properties of solids. San Francisco: Freeman; 1980.

29. Okada T, Kakinuma F, Ohno S. Electronic properties of liquid Cu-Te, Ag-Te, Au-Te and Pb-Te binary alloys. *J Phys Soc Jpn.* 1983;52:3526-35.
30. Schnyders HS, Hahn J, Streutker D, van Zytveld J B. The electronic transport properties of liquid Ag-Te. *J Phys Condens Matter.* 1997;9:10121-8.
31. Shimojo F, Aniya M, Hoshino K. Anomalous cation-cation interactions in molten CuI: ab initio molecular-dynamics simulations. *J Phys Soc Jpn.* 2004;73:2148-53.
32. Shimojo F, Inoue T, Aniya M, Sugahara T, Miyata Y. Ab initio molecular-dynamics study of static structure and bonding properties of molten AgI. *J Phys Soc Jpn.* 2006;75:114602.
33. Stanley HE. Introduction to phase transitions and critical phenomena. Oxford: Clarendon Press; 1971.
34. Glazov VM, Mamedov SM, Burkhanov AS. Analysis of features of the charge transfer mechanism in melts of copper and silver chalcogenides based on studies of electroconductivity and the Hall effect. *High Temp.* 1987;25:369-375.
35. Sharma A, Barman PB. Effect of Bi incorporation on the glass transition kinetics of $\text{Se}_{85}\text{Te}_{15}$ glassy alloy. *J Therm Anal Calorim.* 2009;96:413-7.
36. Saraswat S, Kushwaha SSS. Specific heat studies in a-Se and a- $\text{Se}_{90}\text{M}_{10}$ (M=In, Sb, Te) alloys. *J Therm Anal Calorim.* 2009;96:923-7.

Table 1 Electronegativity values [23] and the electronegativity differences / $\Delta\chi$.

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

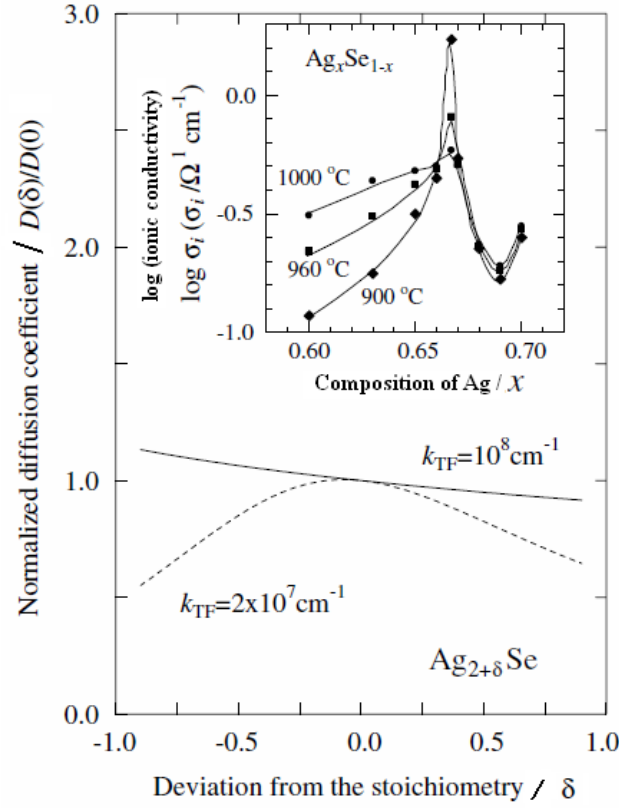


Fig. 1 Composition dependence of the normalized diffusion coefficient $D(\delta)/D(0)$ in liquid $\text{Ag}_{2+\delta}\text{Se}$ as a function of the deviation from the stoichiometric composition δ [19]. The calculated values for two values of Thomas-Fermi screening wave number K_{TF} are shown. The inset shows the experimental results of the ionic conductivity [21]. The stoichiometric composition $\delta=0$ corresponds to $x=0.667$.

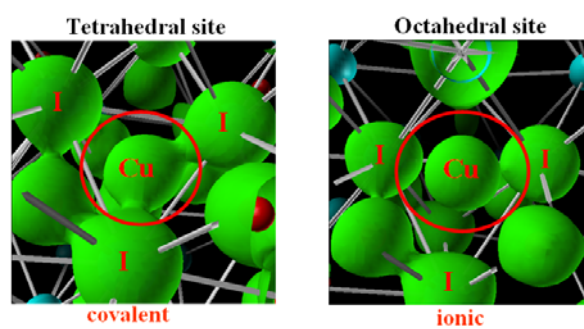


Fig. 2 Isosurface of electron density around the Cu ion at the tetrahedral and octahedral sites [15].

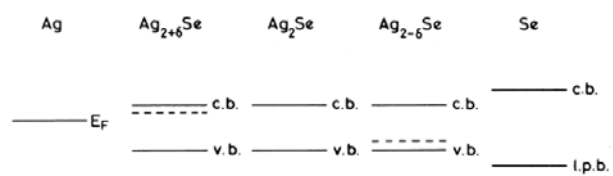


Fig. 3 Schematic representation of the energy diagram in the system Ag-Se.

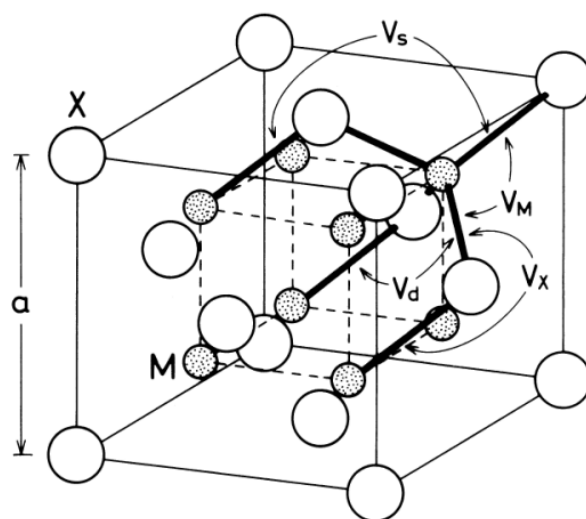


Fig. 4 Antifluorite structure of a M_2X compound. M and X indicate the metal and chalcogen atoms, respectively. The interaction between the bonding orbitals up to second nearest neighbor is shown.

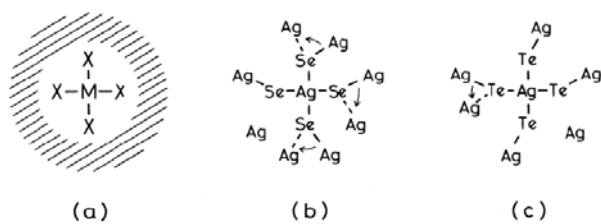


Fig. 5 (a) The connection of X to another M depends on the probability to find M in the hatched region. (b) The bond fluctuation leads to an increase of the coordination number of Ag around Ag. (c) The strong covalency is unfavorable for the bond fluctuations.

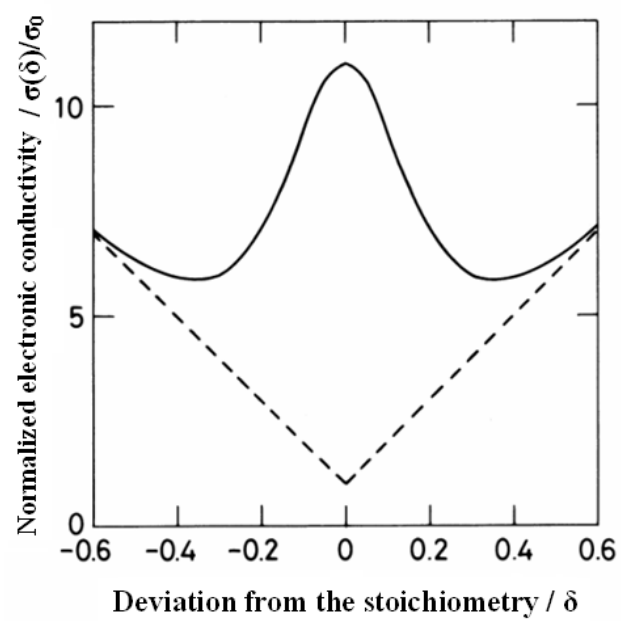


Fig. 6 Schematic representation of the behavior of electronic conductivity in the presence (solid line) and absence (broken line) of bond fluctuation processes.