Ionic Conductivity in Liquid Sn–Se, Sb–Se and Bi–Se Alloys

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Simultaneous measurements of ionic and electronic conductivities around the stoichiometric composition have been carried out on liquid Sn–Se, Sb–Se and Bi–Se alloys by applying the residual potential theory. The ionic conductivity, \( \sigma_i \), in liquid Sn–Se and Sb–Se alloys increases with increasing temperature, while, in liquid Bi–Se alloys, it decreases with increasing temperature. The isothermal \( \sigma_i \) in liquid Sn–Se and Sb–Se alloys at higher temperatures exhibits a minimum at the stoichiometric composition of SnSe and Sb_2Se_3, respectively, and, on the other hand, it shows a maximum at Bi_2Se_3 in liquid Bi–Se alloys. Values of \( \sigma_i \) at SnSe, Sb_2Se_3 and Bi_2Se_3 near the melting temperature are 7.40 Sm\(^{-1}\) at 1173 K, 0.448 Sm\(^{-1}\) at 893 K and 45.3 Sm\(^{-1}\) at 993 K, respectively, which are about two orders of magnitude smaller than the corresponding electronic conductivities, \( \sigma_e \). The value of \( \sigma_i \) of liquid Bi_2Se_3, which is the largest among three liquids, is roughly comparable to that for ionic liquid alloys such as Ag and Tl-chalcogenides. In contrast, liquid Sb_2Se_3 indicates the smallest \( \sigma_i \) due to the strong covalent bonding between unlike atoms. The minimum of the \( \sigma_i \)-isotherm at SnSe and Sb_2Se_3 in liquid Sn–Se and Sb–Se alloys also reflect the covalent nature in these liquids.

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1. Introduction

It has been well known that liquid metal-chalcogen alloys exhibit common semiconducting behaviors at the stoichiometric composition, such as deep minima of the electronic conductivity, \( \sigma_e \), and electronic paramagnetic susceptibility, \( \chi_e \), and a reverse of the sign in the thermoelectric power, \( S \). These behaviors have successfully been interpreted in the term of the electronic localization theory based on the strongly scattering regime for electrons. Usuki, one of the present authors, has firstly measured the ionic conductivity, \( \sigma_i \), over a whole range of composition in Ti–Se liquid alloys, and observed a sharp maximum of \( \sigma_i \) at the stoichiometric composition of Ti_2Se. The coexistence of \( \sigma_e \)-minimum and \( \sigma_i \)-maximum at the stoichiometric composition has also been found in liquid Ag–TlSe and Ag–Te alloys. In these systems, it has been considered that the effect of the electron-ion cross conduction caused mainly by the electrostatic interactions, which disturbs smooth migration of mobile ions, is the smallest at the stoichiometric composition, where electrons are strongly localized. However, the conflicting result has recently been reported in liquid Ag–Se alloys, where both \( \sigma_e \) and \( \sigma_i \) exhibit steep maxima at the stoichiometric composition of Ag_2Se, although both maxima gradually disappear with increasing temperature. The simultaneous appearance of \( \sigma_e \)– and \( \sigma_i \)-maxima can not be explained in terms of the ion-electron interaction effect. The authors have suggested that unusual ionic and electronic conductivities observed in liquid Ag–Se alloys are closely related to the inherent structure of liquid Ag_2Se, which maintains the local atomic configuration in the fast-ion crystalline phase (\( \alpha \)-Ag_2Se), particularly, just above the melting temperature.

Information on \( \sigma_i \) in liquid metal-chalcogen alloys containing polyvalent metals are very scarce at present. This paper reports observed results of \( \sigma_i \), together with those of \( \sigma_e \), in the stoichiometric composition range in liquid Sn–Se, Sb–Se and Bi–Se alloys, applying the residual potential method. We also explore the relationship between the ionic conduction and liquid structure in these alloys.

2. Experimental Procedures

Purities of Sn, Sb, Bi and Se used were all better than 99.99%. Alloys with the required composition were prepared by enclosing together elemental components into an evacuated fused quartz ampoule and mixing thoroughly in the molten state. The fused quartz d.c. conductivity cell with four tungsten electrodes was used for the measurement of \( \sigma_i \) and \( \sigma_e \), which is identical to that in our previous measurement. The electrodes were cleaned in advance by the electrolysis in a dilute solution of NaOH. The molten alloy was inserted in the cell under the Ar atmosphere of about 0.1 MPa. The cell constant was determined at room temperature, using purified liquid Hg. The temperature of the sample was measured by the calibrated CA thermocouple attached to the central position of the sample. \( \sigma_i \) and \( \sigma_e \) were separately obtained by employing the residual potential theory developed by Yokota. Essential details of the theory are described as below.

A constant d.c. current is applied to the sample across the electrodes. When mobile ions in the alloy participate in the conduction together with electrons, we can observe the potential decay process immediately after switching on and off. \( \sigma_i \) is directly obtained from the steady-state potential, \( V_s \), according to the relation, \( V_s = lj/\sigma_e \), where \( j \) and \( l \) denote the current density and distance between electrodes, respectively. \( \sigma_i \) relates to the residual potential at the instant of switching off, \( V_r \), through the equation of \( V_r = \sigma_i/\sigma_e \). Thus, if \( V_r \) is enough large to be deduced from the potential decay curve, \( \sigma_i \) can be calculated from the ratio of \( V_r/\sigma_e \).

The magnetic susceptibility, \( \chi \), of alloys was measured by the Faraday method, using the torsion balance. Details for the measurement have been described previously.

3. Experimental Results

Figure 1 shows the temperature dependence of $\sigma_i$ in liquid Sn–Se, Sb–Se and Bi–Se alloys, respectively. Usuki has pointed out in liquid Tl–Se alloys that the temperature change of $\sigma_i$ near the stoichiometric composition does not necessarily follow the simple thermal activation process. The present $\sigma_i$ at the stoichiometric composition of SnSe in liquid Sn–Se alloys depends little on temperature. In liquid Bi–Se alloys $\sigma_i$ has rather the negative temperature dependence at any composition covered, being consistent with that observed around Ag$_2$Se in liquid Ag–Se alloys. 4)

Composition dependences of $\sigma_i$ in liquid Sn–Se, Sb–Se and Bi–Se alloys are summarized in Fig. 2. Most of $\sigma_i$, which have been hitherto observed in liquid metal-chalcogen alloys, take the sharp maximum at the stoichiometric composi-

![Fig. 1 1/T plots of ionic conductivities, $\sigma_i$, in liquid Sn-Se (a), Sb-Se (b) and Bi-Se (c) alloys, respectively.](image)
Both temperature and composition dependences of isothermal $\sigma_e$ in liquid Sn–Se, Sb–Se and Bi–Se alloys are given in Figs. 3 and 4, respectively. Although $\sigma_e$ in liquid metal-chalcogen alloys usually exhibits a minimum at the stoichiometric composition due to the electron localization, the minimum of $\sigma_e$ in liquid Sb–Se and Bi–Se alloys is less clear owing to extremely low values of $\sigma_e$ at the Se-rich side.

4. Discussions

4.1 Ionic conductivity

Assuming that all metallic atoms in the alloy are fully ionized and participate in the ionic conduction, the number density, $n_i$, and mobility $\mu_i$ of metal $i$ can easily be calculated using the observed $\sigma_i$, through equation,

\[ \mu_i = \frac{\sigma_i}{en_i} = \frac{\sigma_i}{e\rho_0 x_i}, \]

where $x_i$ and $\rho_0$ denote the atomic fraction of metal $i$ and average number density of atoms in the alloy, respectively. Table 1 lists calculated results of $\mu_i$ in liquid Sn–Se, Sb–Se and Bi–Se alloys, respectively. The value of $\mu_i$ at SnSe and Sb$_2$Se$_3$ are considerably smaller than that reported in liquid monovalent metal-chalcogen alloys with the ionic feature (e.g., $358 \times 10^{-10}$ m$^2$V$^{-1}$s$^{-1}$ at Ag$_2$Se (1173 K), $62 \times 10^{-10}$ m$^2$V$^{-1}$s$^{-1}$ at Ag$_2$Te (1233 K), and $78 \times 10^{-10}$ m$^2$V$^{-1}$s$^{-1}$ at Tl$_2$Se (713 K), respectively). Therefore, liquid SnSe and Sb$_2$Se$_3$ cannot be classified as the ionic liquid and are different from liquid silver-chalcogenides. On the other hand, liquid Bi$_2$Se$_3$ has the same order of magnitude of $\mu_i$ as liquid silver-chalcogenides.

It has often been pointed out that the temperature change...
cancellation of the thermal activation and ion-electron cross conduction effects. Similarly, the temperature dependence of $\sigma_i$ at SnSe and Sb$_2$Se$_3$ in liquid Sn–Se and Sb–Se alloys becomes smaller than that at other compositions. However, in liquid Bi–Se alloys, strong negative $d\sigma_i/dT$ is observed at all compositions covered, which can not be explained at present. The similar negative $d\sigma_i/dT$ has been observed at Ag$_2$Se in liquid Ag–Se alloys.\textsuperscript{4} Usuki \textit{et al.} have interpreted the negative temperature coefficient of $\sigma_i$ in liquid Ag$_2$Se, in connection with the significant change of the local atomic configu-

Fig. 3 1/T plots of electronic conductivities, $\sigma_e$, in liquid Sn–Se (a), Sb–Se (b) and Bi–Se (c) alloys, respectively.
Now we discuss the relationship between the magnitude of $\sigma_i$ (or $\mu_i$) and short-range structure, by using structural data of liquid Sb$_2$Se$_3$ and Bi$_2$Se$_3$.

The crystalline structure of Bi$_2$Se$_3$ is a distorted NaCl type with the partial ionic nature, in which one Bi atom is surrounded by three Se atoms in the intralayer and one Se atom in the neighboring layer (the shorter Bi–Se distance) and 2.5 Se in the neighboring layer (the longer one). Crystalline Sb$_2$Se$_3$ has the same structure type, but the shorter bonds are considerably covalent, while, the bonding between neighboring layers is much looser. Then, crystalline Sb$_2$Se$_3$ seems to be constructed by dimmer molecules, Sb$_4$Se$_6$, as described in Fig. 5.

Neutron diffraction measurements have been made by the authors’ group for liquid Sb$_2$Se$_3$ at 943, 993 and 1043 K, and liquid Bi$_2$Se$_3$ at 1073 K. Pair distribution functions, $g(r)$, are represented in Fig. 6. Provided that the local structural order is unchanged in liquid and crystalline states, the longer Sb (or Bi)-Se bond distance should fall at a little shorter $r$ side of the valley between the first and second peaks in $g(r)$. This valley of $g(r)$ is much shallower in liquid Bi$_2$Se$_3$ than that in liquid Sb$_2$Se$_3$, this means that the contribution of the longer Bi–Se must be significant, whereas, that of the longer Sb–Se one is almost absent.

We now investigate the contribution of Sb (or Bi)-Se bonds in both liquid Sb$_2$Se$_3$ and Bi$_2$Se$_3$ by the least squares fit of the model function to the observed structure factor, $S(Q)$. The following model structure factor, $S_{\text{model}}(Q)$, was employed,

$$S_{\text{model}}(Q) = \sum \sum c_i f_i n_j f_j \exp \left( -\frac{1}{2}l_{ij}^2 Q \right) \sin(Qr_{ij}) ,$$

(2)

where $c_i$, $f_i$, and $n_{ij}$ are the concentration of atom $i$, coherent form factor of atom $i$, and number of atoms $j$ around a given atom $i$, respectively. Parameters $l_{ij}$ and $r_{ij}$ in eq. (2), denote the root mean square displacement and bond distance of $i$–$j$ pairs, respectively. In the present fit, we assumed that the ratio of the longer bond distance of Sb (or Bi)-Se pairs to the shorter one remains constant upon melting, e.g., the same ratio in liquid and crystalline states. Then, only $n_{ij}$, besides $l_{ij}$, becomes variable in the present fit.

Table 2 shows the calculated result of structural parameters.
for both liquids, together with the corresponding ones in the crystal. An agreement of the parameters in liquid and crystalline Bi$_2$Se$_3$ encourages us to believe the presence of some kind of crystalline ionic order in the liquid state. The parameters for liquid Sb$_2$Se$_3$ denote that the nearest neighbor covalent Sb–Se bonds within intra-dimers in Fig. 5 remain strengthened as in crystalline state, and, on the other hand, the longer Sb–Se bonds are considerably lost on melting and the molecular feature with Sb$_2$Se$_6$ dimers is enhanced. This structural change may relate to the smaller $\sigma$ for liquid Sb$_2$Se$_3$ and liquid Bi$_2$Se$_3$ compared with the high-temperature one. According to the neutron diffraction measurement by Itoh $et$ $al.$, the nearest neighbor distance and coordination number in liquid SnSe (283 pm and 3.4, respectively) determined from the position and area of the first peak in $g(r)$ are not closer to those in the high-temperature phase (300 pm and 5.0, respectively), but to those in the low-temperature one (285 pm and 3.0, respectively). Possibly, the minimum of the $\sigma$-isotherm at SnSe in liquid Sn–Se alloys in Fig. 2(a) may reflect the covalent nature in the liquid state.

### 4.2 Electronic conductivity

The $\sigma$-isotherm in liquid metal-chalcogen alloys generally exhibits a deep minimum at the stoichiometric composition due to the occurrence of the electron localization.$^{11}$ However, the minimum of $\sigma$ at Sb$_2$Se$_3$ and Bi$_2$Se$_3$ in liquid Sb–Se and Bi–Se alloys in Figs. 4(b) and (c) is less clear owing to low values of $\sigma$ at the Se-rich side. We have attempted to confirm the occurrence of the electron localization at the stoichiometric composition in the present liquid alloys through the measurement of the magnetic susceptibility, $\chi$, the results are shown in Fig. 7. When conduction electrons are strongly localized at the stoichiometric composition, the observed $\chi$ should exhibit the diamagnetic maximum there, corresponding to a rapid decrease in the electronic paramagnetic contribution. The diamagnetic peak obviously appeared at the stoichiometric composition in these alloys as shown in Fig. 7.

The degree of the electron localization can be quantitatively expressed in terms of the $g$-factor, which is the ratio of the density of electronic states at the Fermi level, $E_F$, to the free electron value. According to the strong scattering regime for electrons,$^{10}$ $\sigma$ can be described as follows,

$$\sigma = e^2 \frac{n_{\text{short}}}{\pi \hbar^2 k_F g^2},$$

(3)

where $a$ is the interatomic distance corresponding to the lowest value of the electron mean free path ($a \approx 300$ pm for liquid selenides), and $k_F$ is the Fermi wave vector.$^{17}$ Assuming that the number of conduction electrons is taken to be two per atom for Sn, three per atom for Sb and Bi, respectively, and two electrons per atom are supplied into the conduction band for Se, we can find $g(1173$ K) $\approx 0.20$ at SnSe, $g(893$ K) $\approx 0.03$ at Sb$_2$Se$_3$ and $g(993$ K) $\approx 0.42$ at Bi$_2$Se$_3$, respectively, using the observed $\sigma$. $g \leq 1/3$ has been taken as the criterion for the electronic localization.$^{16}$ Therefore, it appears that electrons in liquid Sb$_2$Se$_3$ are the most localized, reflecting the strong covalent bonds between unlike atoms.

The degree of the atomic ionization in the alloy can be investigated using observed temperature dependences of $\sigma$, and $\chi$. According to the strong scattering regime for electrons,$^{1}$ the following relation is established between $\sigma$ and $\chi$, through an implicit factor, $N(E_F)$ ($N(E_F)$: the number density of electronic states at $E_F$),

Table 2 Structural parameters within the first two nearest neighbor distances in liquid Sb$_2$Se$_3$ and liquid Bi$_2$Se$_3$ calculated through the least squares fit.

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<th>$r$ (short)/pm</th>
<th>$r$ (long)/pm</th>
<th>$n$ (short)</th>
<th>$n$ (long)</th>
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<tr>
<td>Crystal</td>
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<th>$n$ (short)</th>
<th>$n$ (long)</th>
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<tbody>
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<td>2.3</td>
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<tr>
<td>Crystal</td>
<td>286</td>
<td>330</td>
<td>4.0</td>
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</table>
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\[ \chi = \chi_d + C \sigma_e^{1/2}, \]  

(4)

where \( \chi_d \) represents the total diamagnetic contribution by bound electrons in the alloy. The proportional constant \( C \) depends on the electronic band structure and scattering mechanism of electrons. For example, plots of \( \chi \) vs \( \sigma_e^{1/2} \) in liquid Sn–Se alloys are shown in Fig. 8, from which we can get the value of \( \chi_d \) by the extrapolation of lines to the \( \sigma_e^{1/2} = 0 \) axis.

Figure 9 gives plots of \( \chi_d \) vs. composition in liquid Sn–Se, Sb–Se and Bi–Se alloys, together with \( \chi_{d,\text{ion}} \) calculated from the ionic model;

\[ \chi_{d,\text{ion}} = c_m \chi_M(+) + (1 - c_m) \chi_{Se^{2-}}. \]  

(5)

Ionic susceptibilities of Sn\(^{2+}\), Sb\(^{3+}\), Bi\(^{3+}\) and Se\(^{2-}\) were taken from the table of Selwood.\(^{18}\) The value of \( \chi_d \) at Bi\(_2\)Se\(_3\) in liquid Bi–Se alloys is found near the \( \chi_{d,\text{ion}} \) line, while that in liquid Sn–Se and Sb–Se alloys far away from the \( \chi_{d,\text{ion}} \) line, when the alloy composition approaches the stoichiometric one. The result indicates that metallic ions in the latter two alloys are not fully ionized at the stoichiometric composition. The estimation for the atomic ionization at the stoichiometric composition does not conflict with structural and bonding features in these liquid alloys.

5. Conclusion

The ionic conductivity, \( \sigma_i \), and electronic conductivity, \( \sigma_e \), in the stoichiometric composition range in liquid Sn–Se, Sb–Se and Bi–Se alloys have been measured simultaneously by applying the residual potential theory. The results can be summarized as follows,

(1) \( \sigma_i \) in liquid Sn–Se and Sb–Se alloys increases with increasing temperature, but, in liquid Bi–Se alloys, it decreases with increasing temperature.

(2) The \( \sigma_i \)-isotherm in liquid Sn–Se alloys, and that at high temperatures in liquid Sb–Se alloys exhibit a minimum at stoichiometric compositions of SnSe and Sb\(_2\)Se\(_3\), respectively. In stead, in liquid Bi–Se alloys, it shows a maximum at the stoichiometric composition of Bi\(_2\)Se\(_3\), similar to the case of ionic liquid alloys such as Ag–Se and Tl–Se.

(3) Magnitudes of \( \sigma_i \) in liquid SnSe, Sb\(_2\)Se\(_3\) and Bi\(_2\)Se\(_3\) are found to be 7.40 (1173 K), 0.488 (893 K) and 45.3 Sm\(^{-1}\) (993 K), respectively, which are about two orders of magnitude smaller than \( \sigma_i \) in the corresponding liquids.

(4) \( \sigma_i \) in liquid Bi\(_2\)Se\(_3\) is roughly close to that in liquid Tl\(_2\)Se and Ag\(_2\)Se with the structural ionicity. On the other hand, liquid SnSe and, particularly, liquid Sb\(_2\)Se\(_3\) indicate much lower \( \sigma_i \) because of its covalent nature.
(5) Not only the ion-electron cross conduction effect, but also structural effect should be taken into consideration to discuss the ionic conduction in liquid metal-chalcogen alloys. We must consider the structural effect on $\sigma_i$ in liquid alloys containing polyvalent metals.

REFERENCES

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