Electronic and Ionic Conductivities in the Liquid Ag–TlSe System

Takeshi Usuki, Osamu Uemura, Katsunori Satoh† and Yasuo Kameda

Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Yamagata 990-8550, Japan

Simultaneous measurements of electronic and ionic conductivities have been carried out for the liquid Ag,(TlSe)$_{1-x}$ system with $x=0$ to 0.52, applying the residual potential theory. Both the electronic and ionic conductivities increase with increasing temperature at the whole composition range investigated, except for the latter conductivity at $x=0.50$ (corresponding to the stoichiometric composition of AgTlSe). The system exhibits a deep minimum in the electronic conductivity and sharp maximum in the ionic conductivity at this composition. The maximum value of ionic conductivity in the system is nearly one order of magnitude smaller than the minimum one of electronic conductivity. The value of $g$-factor obtained by the relationship of electronic conductivity and magnetic susceptibility is roughly 0.025 at $x=0.5$ at 773 K, implying the occurrence of the electron localization. Further, the number density and mobility for metal ions in the system were estimated using the observed ionic conductivity under the assumption that all of Ag and Tl atoms in the system are univalent ionized and contribute to the ionic conduction. It has been concluded that the ionic mobility drastically increases, while, conduction electrons are strongly localized, at the stoichiometric composition of AgTlSe in the liquid Ag–TlSe system.

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I. Introduction

It has been well known that liquid metal-chalcogen systems essentially involve both electronic and ionic features, for example, anomalous electronic properties which the system shows at the stoichiometric composition are correlated with the degree of the electron localization$^{(1)}$, while, the ordered structure appearing at this composition has more or less the ionic configuration of atoms$^{(2)}$. Accordingly, it is considered to be much significant to measure ionic properties such as the ionic conductivity, in order to explore the original nature of these systems. In the present study, the simultaneous measurement of electronic and ionic conductivities in the liquid Ag–TlSe system has been attempted applying the residual potential theory.

The authors’ group has already reported that the liquid Ag–TlX (X: Se, Te) system shows drastic anomalies of electronic properties and the ordered structure appears at the stoichiometric composition of AgTlX$^{(3)(4)}$. Therefore, the strong localization for conduction electrons and the active motion of mobile ions may be expected at the stoichiometric composition in this system.

The present paper describes results of electronic and ionic conductivities in the liquid Ag,(TlSe)$_{1-x}$ system with $x=0$ to 0.52. The results provide new sights on the electrical transport mechanism in liquid metal-chalcogen systems.

II. Experimental Procedures

Purities of constituting elements used are all better than 99.99%. Alloys with the required composition were prepared by sealing the starting elements in an evacuated quartz ampoule and reacting thoroughly in the molten state.

The electrical conductivity was measured by a d.c. four-terminal method. The Pyrex glass cell for the measurement, into which four tungsten electrodes are inserted, is illustrated in Fig. 1. The electrodes were cleaned by the electrolysis in a dilute solution of NaOH. The sample was vacuum-sealed in the cell, the resistivity constant of which was in advance measured using the standard sample of purified Hg. The temperature of the sample was determined by a calibrated C–A thermocouple attached to the central position of the sample.

The magnetic susceptibility was measured by the Faraday method using the torsion balance. Details for the susceptibility measurement have already been written in our earlier paper$^{(5)}$.

The ionic conductivity, $\sigma_i$, can be determined employing the residual potential theory for high ionic conductors, which has been treated by Yokota$^{(6)}$. The intensity of the direct current applied is assumed to be too weak to bring on the electrolysis at the boundaries of both electrodes. Now, the direct current with its constant intensity is applied to the sample across the electrodes (see Fig. 1). Immediately after switching on, all of conductive electrons and ions in the system participate in the conduction. The current after the steady state is carried by electrons alone. When the current after such the

† Graduate Student, Yamagata University.
steady state is switched off, the residual potential is left and gradually damped off according to the polarization decay (the decay process).

On the basis of the Yokota’s theory, the potential between two tungsten probes after switching on can be expressed as,

\[ V = -\frac{jl}{\sigma_e} \phi \left( \frac{t}{\tau} \right), \tag{1} \]

where, \( l \) and \( \sigma \) are the distance between two probes and total electrical conductivity \( (\sigma = \sigma_e + \sigma_i) \), respectively, and

\[ \phi \left( \frac{t}{\tau} \right) = -\frac{8}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left[ -(2m+1)^2 \frac{t}{\tau} \right], \tag{2} \]

where \( \tau \) is the decay time. The schematic diagram of potential vs time is given in Fig. 2. In the stationary state \((t = \infty)\), eq. (1) is reduced to

\[ V_s = -\frac{jl}{\sigma_e}. \tag{3} \]

During the polarization decay, the residual potential, \( V_r \), is damped as,

\[ V_r = \frac{\sigma_i}{\sigma} \sigma_e \phi \left( \frac{t}{\tau} \right). \tag{4} \]

At the instant of switching off, eq. (4) is reduced to

\[ V_r^0 = -\frac{\sigma_i}{\sigma} \sigma_e, \tag{5} \]

where \( V_r^0 \) is the potential at the instant of switching off \((t = 0)\) as in Fig. 2. After all, we find that

\[ \frac{V_r^0}{V_s} = \frac{\sigma_i}{\sigma_e} \tau \tag{6} \]

Thus, \( \sigma_e \) can be obtained from \( V_s \) of eq. (3) and \( \sigma_i \) from the ratio, \( V_r^0/V_s \), of eq. (6), if the latter quantity is enough to be observable.

**III. Experimental Results**

Since the higher order Fourier terms \((m > 0)\) of \( \Phi(t/\tau) \) decay out very rapidly compared with the first one \((m = 0)\), eq. (4) may be approximated by the first term,

\[ V_{r(m=0)} = -\frac{\sigma_i}{\sigma} \sigma_e \frac{8}{\pi^2} \exp \left( -\frac{t}{\tau} \right). \tag{4'} \]

Figure 3 describes an example of the decay process of the residual potential, \( V_r \), which varies exponentially according to eq. (4') except for around \( t = 0 \). The value of \( V_{r(m=0)} \) at \( t = 0 \), \( V_r^0 \), necessary for determining \( \sigma_i \), is obtained by extrapolation of the linear in \( V_r \) vs. \( t \) plot to the intercept. The experimental error in \( \sigma_i \) may be estimated to be less than 10%.

Both \( \sigma_i \) and \( \sigma_e \) in the liquid Ag-TlSe system are shown in Figs. 4 and 5 against the reciprocal absolute temperature, \( 1/T \), respectively. \( \sigma_e \) increases with increasing temperature as in the semiconducting behavior. \( \sigma_i \) at most of compositions increases also with increasing temperature.

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**Fig. 3** An example of the decay process of the residual potential.
following the thermal activation process. However, $\sigma_i$ at the stoichiometric composition of AgTlSe ($x=0.5$) is temperature-independent at higher temperatures.

IV. Discussions

Figure 6 plots the composition dependence of $\sigma_e$ at 773 K in the liquid Ag–TlSe system, together with that of $\sigma_i$ at the same temperature. A deep minimum of the isothermal $\sigma_e$ with its value of $1.87 \times 10^5$ S·m$^{-1}$ can be observed at the stoichiometric composition of $x=0.5$, which implies the appearance of the electron localization. The electron localization suddenly begins at about $x \sim 0.4$ near to the stoichiometric composition in Fig. 6.

The feature of the electronic band structure in the liquid state remains unresolved at present. Since constituting atoms or ions are not strictly kept at a certain position and the density fluctuation is predominant in the liquid state, conduction and valence band edges have been said to have a tail into the energy region corresponding to the forbidden band in the crystalline solid. The energy gap between both bands is replaced by the minimum of the density of electronic states at the Fermi level, $E_F$, or the states near $E_F$ are strongly localized due to the disorder. In such the band picture, the $g$-factor denoting the ratio of the real density of electronic states to the free electron value is available as the measure of the electron localization. According to the strong scattering approximation for conduction electrons, the relationship between the observed $\sigma_e$ and $g$-factor is given as below$^{(6)}$,

$$\sigma_e = \frac{e^2 n^{2/3} \hbar}{(3\pi^2)^{1/3}} g^2,$$

(7)

Fig. 4 The electronic conductivity, $\sigma_e$, in the liquid Ag$_x$(TlSe)$_{1-x}$ system as a function of temperature.

Fig. 5 The ionic conductivity, $\sigma_i$, in the liquid Ag$_x$(TlSe)$_{1-x}$ system as a function of temperature.

Fig. 6 Composition dependences of both electronic and ionic conductivities at 773 K in the liquid Ag$_x$(TlSe)$_{1-x}$ system.
where, \( n \) is the number density of conduction electrons and \( a \) is the average interatomic distance taken for the lowest value of the electron mean free path, which can be approximated to be \(-3 \times 10^{-10} \text{ m}\) in liquid selenides. If knowing \( n \), the value of \( g \) can be estimated by eq. (7) using the observed \( \sigma_d \). The estimated \( g \)-factor at 773 K in the liquid Ag–TlSe system is given in Fig. 7, where the assumption that Ag, Tl and Se supply 1, 1 and 2 electrons per atom into the conduction band was used for determining \( n \). The condition of \( g \leq 1/3 \) has often been employed as the criterion of the electron localization, that is to say, the minimum of the density of electronic states occurs at this condition\(^7\). \( g = 0.025 \) at \( x = 0.5 \) in the present system is appeared to be considerably lower than the critical value.

In Fig. 6, it is of particular interest that \( \sigma_d \) has a steep maximum at \( x = 0.5 \), in which \( \sigma_d \) falls into minimum. The value of \( \sigma_d \) at 773 K at this composition is \( 1.66 \times 10^3 \text{ S} \cdot \text{m}^{-1} \), which is nearly one order of magnitude smaller than the minimum value of \( \sigma_d \). The appearance in “high ionic conduction” at the stoichiometric composition, where the electron localization strongly occurs, has been previously observed in the liquid Tl-Se system by one of the present authors\(^8\). Assuming that Ag and Tl are univalently ionized and all of them participate in the conduction, ionic transport parameters in the liquid Ag–TlSe system can roughly be calculated by the following equations,

\[
n_i = \frac{\rho}{M} N_A x_i \quad \text{and then,} \quad \mu_i = \frac{\sigma_i}{en_i},
\]

where, \( n_i, \mu_i, \rho, M, N_A \) and \( x_i \) denote the number density of ions, ionic mobility, bulk density and mass of the alloy, Avogadro number and sum of the atomic fraction of Ag and Tl, respectively. Table 1 lists the calculated values of \( n_i \) and \( \mu_i \) in the liquid Ag–TlSe system using the observed \( \sigma_d \). It is suggested that a rapid rise in \( \mu_i \) at \( x = 0.5 \) brings the maximum of \( \sigma_d \) in Fig. 6.

When the ionic ordered structure is formed and the density fluctuation falls into minimum at the stoichiometric composition, it can reasonably be understood that the isothermal \( \sigma_d \) takes a minimum value at this composition, because valence electrons are strongly bound by atoms and ions due to the formation of the compound\(^9\). On the contrary, particularly from the point of solid-state physics, it is difficult to explain that \( \sigma_d \) (or \( \mu_i \)) has a maximum value at the compound-forming composition. In practice, the ionic conduction in solid ionic compounds is rather stimulated by the structural disorder such as vacancies and interstitial sites. However, the situation concerning the ionic conduction in the liquid state may be supposed to be considerably different from the solid one. Since various spaces necessary to the diffusion of mobile ions are always prepared in the liquid state, the structural disorder may be expected to disturb the diffusive motion of ions.

The high temperature phase of crystalline Ag₆X (X: the chalcogen atom) is well known to be a high ionic conductor due to mobile Ag⁺ tetrahedrally surrounded by X\(^{\text{2-}}\). Ag⁺ in crystalline AgTlX is also surrounded tetrahedrally by X with similar Ag⁺-X distances to c-Ag₆₂X\(^{\text{11}}\). Tl⁺ is located adjacent to X in the open channel between long chains formed by corner sharing AgX₄/2 tetrahedra. The authors’ group has previously reported that the network structure by AgTe₄/2 tetrahedra in crystalline AgTlTe substantially remains on melting\(^9\). Although there is no structural information on liquid AgTlSe, it seems reasonable that the maximum value of \( \mu_i \) at the stoichiometric composition in the liquid Ag–TlSe system is correlated with the appearance of c-AgTlX-like ordered structure, where Se is regularly located and more spaces to which Ag⁺ and Tl⁺ transfer are sufficiently ready. However, it should be kept in mind again that the derivation of \( \mu_i \) listed up in Table 1 is based on the assumption that all of constituting metal atoms in the system are univalently ionized in the whole composition range covered. Particularly, values of \( \mu_i \) in the TlSe rich region in Table 1 are only reference figures, because this assumption is not strictly acceptable, from
both points of view of the valence of Tl and full ionization of metal atoms.

The degree of the ionization of constituting atoms in the system can be investigated through the relationship between \( \sigma_e \) and \( \chi \) (the magnetic susceptibility). In the strong scattering approximation for electronic conductors with \( q \leq 1/3 \), \( \sigma_e \) is proportional to the square of the density of electronic states at \( E_F \), \( N(E_F) \), while, the electronic term in total \( \chi \) is roughly proportional to \( N(E_F) \), and then, the following equation stands between \( \sigma_e \) and \( \chi \) through an implicit factor, \( N(E_F)^{1/2} \),

\[
\chi = \chi_\text{d} + C \sigma_e^{1/2},
\]

(9)

where, \( \chi_\text{d} \) means the total diamagnetic contribution by bound electrons in the system. A proportional constant, \( C \), depends on the electronic band structure and scattering mechanism of conduction electrons. Figure 8 plots \( \chi_\text{d} \) (the observed \( \chi \) per g-atom) against \( \sigma_e^{1/2} \) in the liquid Ag-TISe system. We can find \( \chi_\text{d} \) (\( \chi \) per g-atom) by the extrapolation of lines to the \( \sigma_e^{1/2} = 0 \) axis. Figure 8 involves \( \chi_{\text{d,ion}} \) given by the ionic model as below,

\[
\chi_{\text{d,ion}} = - \frac{1}{2 - x} \left\{ x \chi_{\text{Ag}^+} + (1 - x) \chi_{\text{Tl}^+} + (1 - x) \chi_{\text{Se}^2-} \right\}.
\]

(10)

Ionic susceptibilities of Ag\(^+\), Ti\(^+\) and Se\(^2-\) were respectively referred from the table by Selwood\(^{13}\). It appears in Fig. 8 that the value of \( \chi_\text{d} \) approaches the ionic model (the broken curve) when the alloy concentration comes near \( x = 0.5 \), that is to say, Ag, TI and Se in the stoichiometric composition range reasonably lie in +1, +1 and \(-2\) ionic states, respectively. Therefore, the calculated value of \( \mu_1 \) in Table 1 may be considered to be acceptable in this range. After all, the maximum of \( \sigma_1 \) observed at the stoichiometric composition is considered to result from a rapid rise of \( \mu_1 \). On the other hand, \( \chi_{\text{d}} \) in the TISe rich region deviates largely from the ionic model possibly because the system is rather covalent or an about half of TI is in the trivalent state. In this result, numerals of \( n_1 \) and \( \mu_1 \) with \( x \leq 0.4 \) in Table 1 are questionable and no more than the reference value as well as that of the \( g \)-factor in Fig. 8 derived regarding the valence of all TI as unity.

V. Conclusion

Simultaneous measurements of electronic and ionic conductivities, \( \sigma_e \) and \( \sigma_1 \), in the liquid Ag\(_x\)(TISe)\(_{1-x}\) system with \( 0 \leq x \leq 0.52 \) have been carried out applying the residual potential theory. The results can be summarized as follows,

1. Both \( \sigma_e \) and \( \sigma_1 \) in the system increase with increasing temperature as expected in the thermal activation process, except for \( \sigma_1 \) at \( x = 0.5 \) at high temperatures.
2. A deep minimum of \( \sigma_1 \) and sharp maximum of \( \sigma_e \) were observed at \( x = 0.5 \), corresponding to the stoichiometric composition of AgTISe, respectively. The maximum value of \( \sigma_1 \) is nearly one order of magnitude smaller than the minimum one of \( \sigma_e \).
3. The minimum of \( \sigma_1 \) reflects the occurrence of the strong electron localization at the stoichiometric composition. The \( g \)-factor calculated in the strong scattering approximation for conduction electrons is below 0.05 at 773 K around \( x = 0.48 \sim 0.52 \), which is much lower than the critical one for the electron localization, \( g \sim 1/3 \).
4. The maximum of \( \sigma_1 \) at \( x = 0.5 \) may be attributable to a rapid rise of the ionic mobility.
5. The magnitude of diamagnetic susceptibility term in the system obtained from the relationship of the observed \( \sigma_1 \) and \( \chi \) suggests that the system becomes ionic when the alloy concentration comes near the stoichiometric composition, while, the covalency is rather predominant in the TISe rich composition range.

REFERENCES