Electronic Properties of Liquid Ag-TlSe System

Yoshinobu Sugawara[†], Hideaki Kudo, Yasuo Kameda
and Osamu Uemura

Department of Chemistry, Faculty of Science, Yamagata University, Yamagata 990, Japan

The electrical conductivity, magnetic susceptibility and thermoelectric power in the liquid Ag-TlSe system have respectively been measured as a function of composition over a wide temperature range. The behavior of these electronic properties is on the whole similar to that in the liquid Ag-TlTe system previously reported; that is to say, the rapid drop of conductivity, appearance of diamagnetic maximum and reverse in sign of the thermoelectric power were observed at the stoichiometric composition of AgTlSe. However, significant differences also appear in both systems, as mentioned below. A main difference is that the magnitude of conductivity minimum at the composition of AgTlSe is smaller than that at the composition of AgTlTe in the liquid Ag-TlTe system. Corresponding to this, the maximum value of thermoelectric power reaches as large as $300 \mu\text{VK}^{-1}$ in the present system, which is compared with $160 \mu\text{VK}^{-1}$ in the telluride one. These results indicate that Ag-Se bonds are stronger than Ag-Te bonds in the liquid chalcogenide solutions. In addition, it should be noted that the composition dependence of conductivity in the TlSe-rich region in the present system is much smaller than the case of the telluride system. The value of overall diamagnetic contribution determined using the conductivity and susceptibility data suggests that the present system indicates a covalent character, particularly, near the composition of AgTlSe. It may be considered that the covalent Ag-Se bonds in crystalline AgTlSe remain undestroyed when melting.

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I. Introduction

Liquid alloy systems consisting of Ag, Tl and Te such as Ag+Te, Ag+TlTe and Ag+AgTlTe₂ have exhibited interesting anomalies of electronic properties at particular compositions⁽¹⁾⁽²⁾. The bonding character between constituting atoms at these compositions has generally been reported to be more or less ionic, that is, Ag, Tl and Te lie in ionic states of +1, +1 and -2, respectively. The more detailed analysis of electronic property data, however, has pointed out that there are slight but significant differences in the bonding character among these alloys, for example, Ag-Te bonds are more covalent in liquid AgTlTe than in liquid Ag₂Te⁽³⁾.

Liquid selenides have a tendency to indicate more covalent and more insulating natures than the corresponding liquid tellurides. Therefore, large differences in composition dependence of the electronic property have often been observed between liquid selenide and telluride systems. For example, electronic properties of the liquid Tl-Te system strongly depend on alloy concentration over a whole composition range, reflecting the variation of the bonding character, while, their composition dependences in the intermediate range in the liquid Tl-Se system are relatively small due to the presence of composition-independent covalent bonds between unlike atoms⁽⁴⁾.

Up to date, common anomalies of electronic properties have been observed in various liquid systems containing metal and chalcogen atoms, such as the deep

minimum of electrical conductivity and diamagnetic peak of magnetic susceptibility. However, we cannot rule out the possibility that a different electronic behavior of which we are not aware will be found out through experiments by new combinations of metal and chalcogen atoms. Therefore, the accumulation of more data is needed to understand fully the electronic behavior of these alloy systems.

The purpose of this paper is to describe measured results of the electrical conductivity, magnetic susceptibility and thermoelectric power in the liquid Ag-TlSe system and to provide a further insight for the electronic behavior of liquid chalcogenide systems. Present results were also compared with the previous data on the liquid Ag-TlTe system in order to discuss the feature of electron localization around the composition where the anomalies occur.

II. Experimental

All samples used in the present work were prepared from 99.999%-purity Ag, 99.95%-purity Tl and 99.999%-purity Se, respectively. Starting mixtures were melted together and then kept in the molten state for more than 48 h in an evacuated quartz ampoule to assure the homogeneity.

The electrical conductivity was measured by an ordinary four-probe direct current compensation method. A conductivity cell with molybdenum electrodes was constructed by a fused quartz tube.

The measurement of magnetic susceptibility was performed by the Faraday method. A Curie-Chenevean

[†] Graduate Student, Yamagata University.

type torsion balance was used to remove the effects of perpendicular forces exerted on the sample such as the buoyancy and thermo-molecular effects.

To obtain the thermoelectric power of the liquid samples, a main furnace moving to the horizontal direction was adopted together with a supplementary heater to introduce the temperature gradient across the sample. The measured thermoelectric voltages representing the thermoelectric power relative to the molybdenum contacts were corrected to give the absolute value using the molybdenum data tabulated by Cusack and Kendall⁽⁵⁾. Measurements of both the conductivity and thermoelectric power were carried out under about 0.1 MPa (1 atm) of Ar. Samples for the susceptibility measurement were sealed into an evacuated quartz cell.

The details of the apparatus and experimental procedure of respective measurements have already been described in the previous papers⁽⁶⁾⁻⁽⁸⁾.

III. Experimental Results

Experimental values of the electrical conductivity, σ , on the cooling process in the liquid Ag-TlSe system are plotted as a function of both temperature and composition in Figs. 1 and 2. The present result of σ for pure TlSe roughly agrees with the previous one by Nakamura and Shimoji⁽⁴⁾, and Rasolondramanitra and Cutler⁽⁹⁾. As often observed in the related liquid systems, the value of

σ for the alloys with more than 50 mol%Ag in the present system disagrees between the heating and cooling processes, perhaps due to the inconsistency in temperature dependence of microscopic structures affecting σ between the two processes.

The temperature dependence of σ for AgTlSe (50 mol%Ag) is slightly larger than that given using data below 844 K by Nakamura *et al.*⁽¹⁰⁾ The satisfactory linearity of $\log \sigma$ vs T^{-1} plots is obtained for the samples with less than 50 mol%Ag, although line-slopes in pure TlSe and 15 mol%Ag alloy strongly depend on temperature below 925 K. This markedly differs from the case of liquid Ag-TlTe system, in which the linear relation between $\log \sigma$ and T^{-1} becomes poor, particularly, at high temperatures because of the rapid enhancement of metallic contribution⁽³⁾. The composition dependence of the activation energy for σ , ΔE_σ , calculated from the linear plots above 925 K is also contained in Fig. 1. ΔE_σ suddenly increases near the composition of AgTlSe owing to the strong localization of carriers. The temporary saturating behavior at considerably high temperatures above 50 mol%Ag does not necessarily mean the full delocalization of valence electrons of electropositive atoms, because the saturation value of σ is smaller in three figures of order than the metallic one.

As shown in Fig. 2, σ decreases gradually by the addition of Ag to liquid TlSe. However, the composition dependence of σ in the low Ag region is considerably weak compared with the case of the liquid Ag-TlTe system⁽³⁾. The relation of electronic property vs composition is generally governed by the composition de-

Fig. 1 Logarithmic plots of electrical conductivity, σ , against the inverse of absolute temperature in the liquid Ag-TlSe system. The figure involves the activation energy for electrical conduction, ΔE_σ , calculated using σ data above 925 K.

Fig. 2 Composition dependence of σ at 973 K and 1173 K in the liquid Ag-TlSe system, respectively. The broken line denotes the result of the liquid Ag-TlTe system (973 K) reported previously⁽³⁾.

pendence of interactions between metal and chalcogen atoms. Therefore, this weak composition dependence of σ in the system seems to suggest that the nonmetallic bonding force between the Tl and Se atoms in the TlSe-rich region is roughly comparable to that of Ag–Se bonds which are predominant in the intermediate composition region. In contrast, it appears in the liquid Ag–TlTe system that the interaction between the Tl and Te atoms in the TlTe-rich solutions is considerably weak compared with that of Ag–Te bonds near the composition of AgTlTe. The minimum of σ in the present system can also be found at 50 mol%Ag, followed by a rapid increase in σ at the excess Ag side, corresponding to the formation of some kind of clusters or chemical short-range orders at this composition.

Figures 3 and 4 give the temperature and composition dependence of atomic magnetic susceptibility, χ_A , in the liquid Ag–TlSe system, respectively. In the figures χ_A means the magnetic susceptibility of assembly with Avogadro number as the sum of numbers of Ag, Tl and Se atoms. Different from the usual behavior in most of liquid semiconductors, the temperature change of χ_A at 50 mol%Ag becomes rather severe at high temperatures, particularly above 1023 K. This exceptional behavior of χ_A has often been observed when chain or ring clusters in the solution are destroyed by the thermal energy. The composition change of χ_A in the present system corresponds well to the result of σ . The system has a diamagnetic peak at 50 mol%Ag because of having the minimum paramagnetic susceptibility of conductive carriers.

In Figs. 5 and 6 measured results of the thermoelectric power, S , in the liquid Ag–TlSe system are described as a function of temperature and composition, respectively.

Fig. 3 Magnetic susceptibility per g-atom, χ_A , at respective compositions in the liquid Ag–TlSe system.

The present value of S for pure TlSe is slightly smaller than that observed by Rasolondramanitra and Cutler⁽⁹⁾, e.g., the value of S at 833 K in the present work is $+220 \mu\text{VK}^{-1}$, which is compared with $+246 \mu\text{VK}^{-1}$ in their work.

Analogously to the case of liquid Ag–TlTe system, S in the present system reverses its sign around 50 mol%Ag from positive in the TlSe-rich region to negative in the

Fig. 4 Composition dependence of χ_A at 973 K and 1173 K in the liquid Ag–TlSe system, respectively.

Fig. 5 Thermoelectric power, S , at respective compositions in the liquid Ag–TlSe system.

Fig. 6 Composition dependence of S at 973 K and 1173 K in the liquid Ag-TlSe system.

Ag-rich region. Representing the insulating behavior in the present system, the maximum value of S in the intermediate concentration region reaches $355 \mu\text{VK}^{-1}$ at 973 K, which is much larger than $160 \mu\text{VK}^{-1}$ at the same temperature in the liquid Ag-TlTe system⁽³⁾.

IV. Discussion

For liquid chalcogenides, σ of which falls in the transport range by the diffusive motion of carriers (below $3 \times 10^5 \text{ Sm}^{-1}$), the following equation for σ can be applied⁽¹¹⁾,

$$\sigma = A[N(E_F)]^2, \quad (1)$$

where, $N(E_F)$ is the temperature-dependent density of states for carriers at the Fermi level, E_F , and a constant A relates to the transport mechanism of carriers. The magnetic susceptibility, χ , is also connected to $N(E_F)$ as below in the delocalized approximation,

$$\chi = \chi_d + \mu_B^2 B N(E_F). \quad (2)$$

Here, χ_d denotes the overall diamagnetic susceptibility in the solution and a coefficient B depends on the band structure near E_F . According to eqs. (1) and (2),

$$\chi = \chi_d + \mu_B^2 \frac{B}{A^{1/2}} \sigma^{1/2} \quad \text{is reduced.} \quad (3)$$

Figure 7 plots the relationship between χ_A and $\sigma^{1/2}$ in the liquid Ag-TlSe system. The value of χ_d has been employed as a measure on the bonding character in the solution. It can be determined by extrapolating lines in Fig. 7 to $\sigma^{1/2}=0$ axis through eq. (3). The previous reports regarding χ_d in liquid chalcogenides obtained in this way are often conflicting, *e.g.*, χ_d for liquid Te has

Fig. 7 Relationship between χ_A and $\sigma^{1/2}$ in the liquid Ag-TlSe system. The dotted line gives the previous result of liquid AgTlTe⁽³⁾. The figure involves the composition dependence of χ_d .

been reported to be $-4.58 \times 10^{-10} \text{ m}^3 \text{ mol}^{-1}$ by Okada *et al.*⁽¹²⁾ and $-5.28 \times 10^{-10} \text{ m}^3 \text{ mol}^{-1}$ by Gardner and Cutler⁽¹³⁾. This disagreement may probably be caused when it is less clear whether a linear relationship between χ and $\sigma^{1/2}$ decided by both χ and σ data correctly stands or not up to the low $\sigma^{1/2}$ side with no data. However, since the extrapolation range is sufficiently narrow at any composition in the present system, we attempt to determine χ_d in this way, the result of which is involved with composition as a variable in Fig. 7. The value of atomic diamagnetic contribution, χ_{dA} , begins to rise rapidly near 40 mol%Ag and reaches a maximum at 50 mol%Ag owing to the strong localization of carriers. This composition dependence of χ_{dA} corresponds well to that of ΔE_g in Fig. 1 which gives the band gap energy.

The magnitude of χ_{dA} at 50 mol%Ag (corresponding to the stoichiometric composition of AgTlSe) obtained by extrapolating the line in Fig. 7 is $-4.25 \times 10^{-10} \text{ m}^3 \text{ mol}^{-1}$, which is 4~5% smaller than $-4.44 \times 10^{-10} \text{ m}^3 \text{ mol}^{-1}$, one third of the sum of molar ionic diamagnetisms of Ag^+ , Tl^+ and Se^{2-} tabulated by Selwood's table⁽¹⁴⁾. The deviation between the two values is almost identical to the case in liquid AgTlTe which has covalent Ag-Te bonds⁽²⁾. Therefore, it may possibly be supposed that liquid AgTlSe has also a covalent nature. According to the study of Tedenac *et al.*⁽¹⁵⁾, crystalline AgTlSe is constructed by distorted AgSe_4 tetrahedra, in which the Ag-Se distance is equal to the ideal covalent one, while, Tl and Se atoms are separated by a longer distance than the Ag-Se distance. From this bonding feature in the crystal, the covalent nature in liquid AgTlSe can be expected to be derived not by the bonding

character of Tl-Se pairs but by that of Ag-Se ones, because electronic properties of this compound change little on melting.

The gradient of the line denoting $BA^{-1/2}$ in Fig. 7 becomes smaller when the composition of alloys comes near 50 mol%Ag, implying either a larger A or smaller B . Assuming that there is little difference in B at all compositions investigated, it is proved according to eq.(1) that the value of $N(E_F)$ markedly reduces at 50 mol%Ag where A is larger and, besides, σ has the minimum. When A is assumed to remain unchanged against composition, a smaller value of B results in the reduction of carrier paramagnetic term. In any way, the gradient of lines in Fig. 7 gives that the strong localization of carriers occurs in the vicinity of the composition of AgTlSe. Further, it is evident from the comparison of line-slopes between liquid AgTlSe and AgTlTe that conductive carriers in the former liquid are more strongly bound into covalent orbitals than in the latter one.

A more quantitative estimate with respect to the degree of carrier localization is to calculate the g -factor, which is the ratio of real density of states for electrons at E_F to the free electron one. In the strong scattering regime for electrons in the system, σ is written as follows⁽¹⁶⁾:

$$\sigma = \frac{e^2}{3\pi^2\hbar} \cdot \Lambda \cdot k_F^2 \cdot g^2, \quad (4)$$

where, k_F and Λ are respectively the Fermi wave vector and the lowest value of carrier mean free path which corresponds roughly to the nearest interatomic distance. The value of g for liquid AgTlSe can be calculated under the following assumptions using the experimental result of σ : The value of Λ is taken to be the covalent Ag-Se distance, 260 pm, and the number of electrons into the conduction band is one per atom for Ag and Tl, and two for Se at the composition of AgTlSe. We find $g=0.09$ at 973 K, which is compared with the value, 0.13, for liquid AgTlTe⁽³⁾.

When the electron density of states at E_F is deep enough to give rise to the localization, the electrical conduction is brought about by carriers excited into extended states, that is to say, the pseudo-gap model is rather proper for the discussion of transport properties in the system. $g=0.3$ has been estimated as the critical value on the occurrence of carrier localization on the basis of the Anderson model⁽¹⁷⁾. This yields $\sigma=3.20 \times 10^4 \text{ Sm}^{-1}$ as the border value between metallic and nonmetallic conduction. The magnitude of σ at all compositions investigated in the present system is smaller than the border value.

According to the single band model⁽¹⁸⁾, the following relationship between σ and S is given through equivalent activation energies, $\Delta E_\sigma = \Delta E_S$:

$$\ln \sigma = \ln \sigma_0 - \frac{e}{k_B} |S| + A_v, \quad (5)$$

where a constant A_v depending on the scattering mechanism can roughly be taken to be unity in the disor-

Fig. 8 Plots of $\log \sigma$ vs S in the liquid Ag-TlSe system. The broken line indicates an ideal slope of eq.(5), $e(2.303k_B)^{-1}$.

dered system. Figure 8 gives plots of $\log \sigma$ vs S in the liquid Ag-TlSe system except for the data of more than 50 mol%Ag alloys, which seem not to obey the single band scheme. As found in most of the liquid chalcogenides, the lines for TlSe rich alloys in Fig. 8 have nearly the same gradients or a little larger ones than the theoretical value, $e(2.303k_B)^{-1}(\Delta E_\sigma \geq \Delta E_S)$. On the other hand, data-points for more than 40 mol%Ag alloys, in which the carrier localization strongly occurs, fall upon the lines with a smaller slope than the theoretical value, i.e., $\Delta E_\sigma < \Delta E_S$. A similar behavior has also been observed in the liquid Ag-TlTe system⁽³⁾. The relation, $\Delta E_\sigma < \Delta E_S$, seems presumably to imply the destruction of AgSe_4 tetrahedron structure forming chains in the system, that is to say, the enhancement of carrier electrons by the formation of dangling bonds shifts S negatively and then ΔE_S apparently becomes larger. Studies about the temperature variation of local order in the present system would be expected in the near future to evidence such destruction of AgSe_4 structural units.

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