

## Electrical properties of molten CuCl-Cu<sub>2</sub>Se mixtures

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**Abstract.** The electrical conductivity,  $\sigma$ , and the thermoelectric power,  $S$ , have been measured for molten CuCl-Cu<sub>2</sub>Se mixtures as a function of composition and temperature. The electrical conductivity of their mixtures decreases rapidly with the addition of CuCl to liquid Cu<sub>2</sub>Se. The thermoelectric power of molten CuCl-Cu<sub>2</sub>Se mixtures shows a steady increase with increasing the composition of CuCl. The experimental results suggest that the dominant transport process in the molten CuCl-Cu<sub>2</sub>Se mixtures changes from electronic to ionic conduction. The composition dependence of  $\sigma$  and  $S$  was analyzed by using the fundamental equation of electrical current densities due to the electrons and the ions. According to this analysis, the conductivity gap increases gradually on the addition of CuCl to liquid Cu<sub>2</sub>Se and the conductivity gap is about 0.68 eV for molten (CuCl)<sub>0.3</sub>(Cu<sub>2</sub>Se)<sub>0.7</sub> mixture.

### 1 Introduction

A decade ago Hamilton *et al.* [1] have determined the structure of liquid Cu<sub>2</sub>Se by neutron diffraction with isotopic substitution. They have indicated that the structure of liquid Cu<sub>2</sub>Se is characterized as an ionic melt consisting of the disordered Cu<sup>+</sup> ions and a more ordered Se<sup>2-</sup> sub-structure. However liquid Cu<sub>2</sub>Se has a significant electronic conductivity of about 158  $\Omega^{-1}\cdot\text{cm}^{-1}$  that originates from the small energy gap [2]. This electronic conductivity dominates the relative small contribution of the ionic conductivity of about 7  $\Omega^{-1}\cdot\text{cm}^{-1}$  to the total conductivity [3]. It is expected that the addition of a noble metal halide to liquid Cu<sub>2</sub>Se results in the rapid decrease in the electronic conductivity. Eventually, at sufficiently high halide compositions the electronic conduction becomes comparable and then less than the ionic conduction so that the mixture begins to show electrical properties more typical of a normal molten salt.

The electrical conductivity of molten CuCl lies in the range from 3.6 to 4.1  $\Omega^{-1}\cdot\text{cm}^{-1}$  at the temperature up to 1173 K and may be conceived as the super ionic conductors with the activation energy for mobile Cu<sup>+</sup> ions [4]. Molten CuCl has a positive and large thermoelectric power due to the dominant transport process of Cu<sup>+</sup> ions. Therefore, the transport process in the molten CuCl-Cu<sub>2</sub>Se mixture changes from ionic to electronic with the addition of Cu<sub>2</sub>Se to CuCl. We attempt to study the change in the thermoelectric power of this mixture with increasing the electrical conductivity.

Liquid Ag<sub>2</sub>Se has long been known to show the negative temperature coefficient of the conductivity

observed in the stoichiometric composition [2,5,6]. The conductivities of (AgCl)<sub>1-c</sub>(Ag<sub>2</sub>Se)<sub>c</sub> with  $c \geq 0.7$  also decrease with increasing temperature. For molten AgCl-Ag<sub>2</sub>Se the thermoelectric power on the AgCl side starts positive, shows a *p-n* transition at  $c \sim 0.2$ , reaches its deep minimum at  $c = 0.4$  and becomes conventional negative on the Ag<sub>2</sub>Se-rich side [7]. We will also make the comparisons of contrasting results between molten CuCl-Cu<sub>2</sub>Se and AgCl-Ag<sub>2</sub>Se systems.

### 2 Experimental procedure

Electrical conductivity and thermoelectric power measurements were made on molten CuCl-Cu<sub>2</sub>Se mixtures simultaneously using a quartz cell system as described previously [7]. In this system small tapered graphite electrodes in direct contact to molybdenum bands and wires were used to make the electrical conductivity and thermoelectric power measurements. In order to prevent evaporation and oxidation, the experiments were carried out in a pure argon atmosphere. To ensure good mixing and to remove any bubbles that formed in the sample, the sample could be agitated using a thin quartz rod. For the chloride rich compositions the thermoelectric power experiments were also carried out using an identical arrangement except that the tapered graphite electrodes were replaced by similar pure copper electrode. All the temperature measurements were made using type K (Chromel-Alumel) thermocouples placed in direct contact with the molybdenum bands immediately above the electrodes.

The thermoelectric power measurements were made

using the  $\Delta T$  method as outlined previously [7]. The thermoelectric power measurements were using copper electrodes for composition  $c \leq 0.7$  in order to avoid erroneous measurements due to the contact potentials between the electrode and the liquid. For  $\text{Cu}_2\text{Se}$  the thermoelectric power was measured using graphite electrodes as its melting temperature (1403 K) is above the melting temperature of pure copper (1358 K). Accurate control of the temperature of sample was achieved by using a two zone furnace. The thermoelectric emf's were measured using a high impedance digital voltmeter with a 10 nV accuracy. The absolute thermoelectric power of the sample was calculated after correction for an absolute thermoelectric power of the molybdenum [8]. A master alloy of  $\text{Cu}_2\text{Se}$  was prepared from elemental pure Cu (99.99%) and Se (99.999%) of the appropriate mass, sealed in a silica tube and heated in a furnace at 1473 K for three hours. Pure CuCl was obtained from Wako Pure Chemical Industries Ltd.

### 3 Experimental results

Figure 1 shows the electrical conductivity,  $\sigma$ , as a function of temperature for molten  $\text{CuCl-Cu}_2\text{Se}$  mixtures. The value of  $\sigma$  for liquid  $\text{Cu}_2\text{Se}$  reported in refs. 9, 10, 2 and 3 is 117, 131, 158 and 162  $\Omega^{-1}\cdot\text{cm}^{-1}$  at the melting point, respectively [2,3,9,10]. The origin of the wide range of values reported for this material is undoubtedly due to the rapid change in  $\sigma$  with composition observed around the stoichiometric composition and the difficulty in maintaining strict stoichiometry due to the evaporation of Se from the sample. The data of Okada and Ohno were obtained at a pressure of 10 bar [9]. In this work, we find 130  $\Omega^{-1}\cdot\text{cm}^{-1}$  at the melting point. The value of  $\sigma$  for molten CuCl is in good agreement with the value obtained by Garbee and Flengas [4]. The temperature

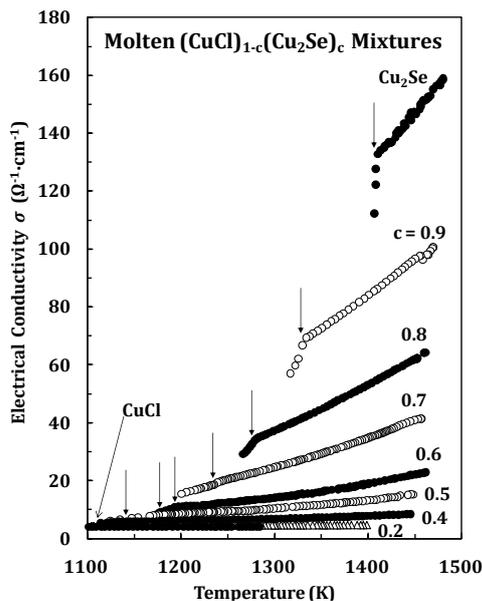


Fig.1 Electrical conductivity,  $\sigma$ , of molten  $\text{CuCl-Cu}_2\text{Se}$  mixtures as a function of temperature. The arrows indicate the melting point of the mixture. The experimental error is about  $\pm 2\%$ .

coefficient of electrical conductivity was found to be positive at all compositions.

Figure 2 shows the thermoelectric power,  $S$ , as a function of temperature for molten  $\text{CuCl-Cu}_2\text{Se}$  mixtures. The value of  $S$  was found to be positive at all compositions. The experimental results for molten  $(\text{CuCl})_{1-c}(\text{Cu}_2\text{Se})_c$  with  $c \leq 0.7$  are obtained with reference to Cu electrodes. The data of  $S$  for liquid  $\text{Cu}_2\text{Se}$  correspond to those obtained with reference to graphite electrodes and we find a value of 152  $\mu\text{V/K}$ , compared to the values of 172  $\mu\text{V/K}$  and 40  $\mu\text{V/K}$  at the melting point as reported by Enderby and Barnes, Okada and Ohno, respectively [2,9]. According to Okada and Ohno there is evidence of a  $p-n$  transition taking place close to the stoichiometric composition and the large variation in  $S$  reported here may again be associated with the rapid changes in  $S$  that occur with small changes in composition near the  $p-n$  transition [2].

Figure 3 shows a comparison between the composition dependence of  $\sigma$  for molten  $\text{CuCl-Cu}_2\text{Se}$  and  $\text{AgCl-Ag}_2\text{Se}$  mixtures. The  $\sigma$  of molten  $\text{CuCl-Cu}_2\text{Se}$  mixtures decreases rapidly as the CuCl is added. This composition dependence of  $\sigma$  is much smaller than that for  $(\text{AgCl})_{1-c}(\text{Ag}_2\text{Se})_c$  over the wide composition range  $c \geq 0.3$ . This suggests that the chemical bonds in molten  $\text{CuCl-Cu}_2\text{Se}$  are more stable than those in molten  $\text{AgCl-Ag}_2\text{Se}$  for the whole compositions. Molten  $(\text{AgCl})_{1-c}(\text{Ag}_2\text{Se})_c$  with  $c \geq 0.6$  has a positive temperature coefficient of  $\sigma$ .

Figure 4 shows a comparison between the composition dependence of  $S$  for molten  $\text{CuCl-Cu}_2\text{Se}$  and  $\text{AgCl-Ag}_2\text{Se}$  mixtures. The  $S$  of molten  $\text{CuCl-Cu}_2\text{Se}$  mixtures increases steadily as the CuCl is added. For the  $\text{AgCl-Ag}_2\text{Se}$  system, the transition from dominantly electronic to ionic conduction is observed as a clear sign change in  $S$ . However molten  $\text{CuCl-Cu}_2\text{Se}$  system has the composition dependence without sign change in  $S$ . The data of  $S$  predict that the superficially different transition

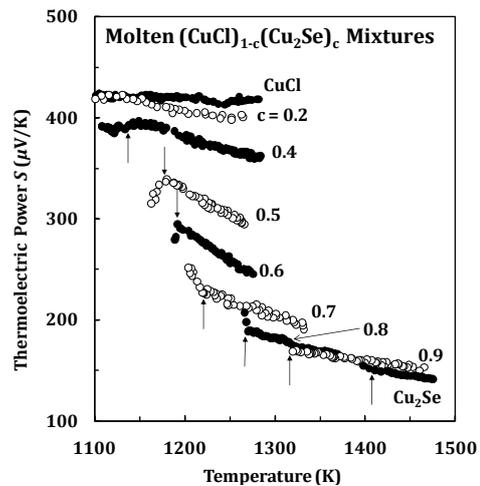


Fig.2 Thermoelectric power,  $S$ , of molten  $\text{CuCl-Cu}_2\text{Se}$  mixtures as a function of temperature. The arrows indicate the melting point of the mixture. The data of  $S$  for mixtures with compositions  $c \leq 0.7$  and  $0.8 \leq c$  were obtained using copper and graphite electrodes, respectively. The experimental error is about  $\pm 8 \mu\text{V/K}$ .

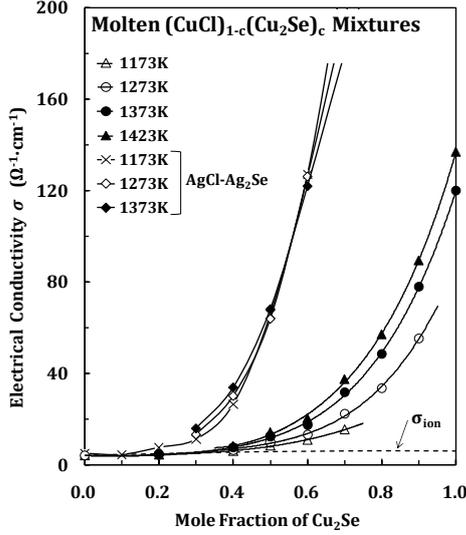


Fig.3 A comparison between the composition dependence of  $\sigma$  for molten CuCl-Cu<sub>2</sub>Se and AgCl-Ag<sub>2</sub>Se mixtures. The dashed line of  $\sigma_{ion}$  is the ionic conductivity of molten CuCl-Cu<sub>2</sub>Se mixtures. The solid lines are guide for eye. The values of  $\sigma$  for molten AgCl-Ag<sub>2</sub>Se were obtained from ref.7.

from dominantly electronic to ionic conduction takes place in the intermediate range.

#### 4 Discussion

Enderby and Barnes have concluded that the values of  $\sigma$  and  $S$  for copper-based chalcogenides can be estimated from the simplified model of energy dependent conductivity [2]. According to the values of  $\sigma$  and  $S$  obtained in this work, liquid Cu<sub>2</sub>Se is liquid semiconductor with a conductivity gap of 0.25 eV. It is easily expected that the conductivity gap of molten CuCl-Cu<sub>2</sub>Se mixtures increases with the addition of CuCl to liquid Cu<sub>2</sub>Se. Molten CuCl is almost purely ionic conductor without any dispute. The electrical property of molten CuCl-Cu<sub>2</sub>Se mixtures would be closely related to both transports due to the conduction electrons and ions in the mixture.

Therefore, the  $\sigma$  and  $S$  of molten CuCl-Cu<sub>2</sub>Se mixtures can be estimated by using the fundamental equation of electrical current densities for electrons and ions as follows [7,11,12],

$$j = j_{el} + j_{ion} = \sigma_{el}[E + (Q_{el}/eT)\nabla T] + \sigma_{ion}[E - (Q_{ion}/eT)\nabla T - (kT/en_i)(\partial n_i/\partial T)\nabla T - \alpha_1\nabla T], \quad (1)$$

where  $\sigma_{el}$  and  $\sigma_{ion}$  are the conductivities due to the electrons and the ions, respectively. The  $Q_{el}/eT$  and  $Q_{ion}/eT$  are the thermoelectric powers due to the electrons and the ions, respectively. It is assumed that the conduction due to the Cl ions can be neglected. The  $n_i$  is the number density of ions. The value of  $\alpha_1$  corresponds to the difference between the electrochemical potentials at the electrodes at the two temperatures.

Putting the temperature gradient  $\nabla T=0$  in eq.(1), the conductivity is given by [7],

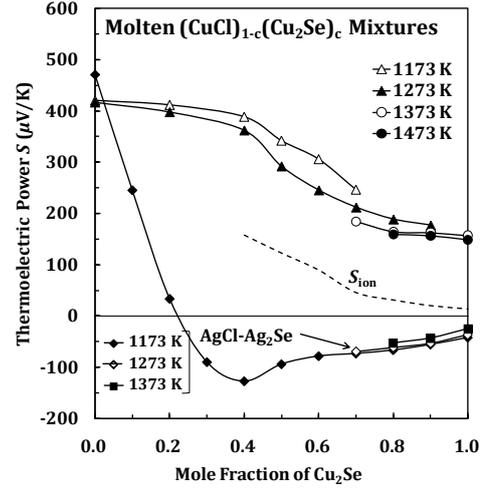


Fig.4 A comparison between the composition dependence of  $S$  for molten CuCl-Cu<sub>2</sub>Se and AgCl-Ag<sub>2</sub>Se mixtures. The value of  $S_{ion}$  was estimated from the assumptions that  $\sigma_{ion}=5.5-7 \Omega^{-1}\cdot\text{cm}^{-1}$  and  $S_{II}$  is 412  $\mu\text{V}/\text{K}$ . The solid lines are guide for eye. The value of  $S$  for molten AgCl-Ag<sub>2</sub>Se were obtained from ref.7.

$$\sigma = \sigma_{el} + \sigma_{ion} = -\int \sigma(E)(\partial f/\partial E)dE + n_i e^2 D_i / kT, \quad (2)$$

where  $\sigma(E)$  is the energy dependent conductivity formed by the valence and conduction bands [2]. The  $D_i$  is the diffusion coefficient of ions.

Putting  $j=0$  in eq.(1), we obtain [7,11,12]

$$S = E/\nabla T = (\sigma_{el}/\sigma)(-Q_{el}/eT) + (\sigma_{ion}/\sigma)[(Q_{ion}/eT) + (kT/en_i)(\partial n_i/\partial T) + \alpha_1], \quad (3)$$

where  $Q_{el}$  is given by [2]

$$Q_{el} = \int \{\sigma(E)/\sigma\}(E-E_F)(\partial f/\partial E)dE. \quad (4)$$

The second term on the right-hand side of eq.(3) has been given by Lidiard and Haga [11,12]. The  $\alpha_1$  is often denoted the inhomogeneous thermoelectric power which can be estimated from the temperature coefficient of electrochemical potential. The electrochemical potential of molten CuCl obtained at 773 K, 1073 K 1273 K is 1.024 V, 0.970 V and 0.943 V, respectively [13]. Therefore, the values of  $\alpha_1$  estimated at 923 K and 1173 K are about 180  $\mu\text{V}/\text{K}$  and 162  $\mu\text{V}/\text{K}$ , respectively.

The ionic conductivity of liquid Cu<sub>2</sub>Se was obtained using the residual current technique by Itoh *et al.* [3]. The ionic conductivity in molten CuCl rich mixtures has been also determined from the temperature dependence of  $\sigma$  [14]. From these results the ionic conductivity was found to be approximately  $7 \Omega^{-1}\cdot\text{cm}^{-1}$  at the melting point for liquid Cu<sub>2</sub>Se and  $4 \Omega^{-1}\cdot\text{cm}^{-1}$  at 1173 K for molten CuCl. We assume that the value of  $\sigma_{ion}$  for the molten mixtures varies linearly from CuCl side to Cu<sub>2</sub>Se side. From this assumption, we obtained the values of  $\sigma_{el}$  of molten mixtures.

The positive and large values of  $S$  for molten CuCl and (CuCl)<sub>1-c</sub>(Cu<sub>2</sub>Se)<sub>c</sub> with  $c=0.2, 0.4$  depend mainly on the second term on the right-hand side of eq.(3). It also

suggests that the dominant transport process is due to the motion of  $\text{Cu}^+$  ions in the molten salts. The decrease in  $S$  for molten  $(\text{CuCl})_{1-c}(\text{Cu}_2\text{Se})_c$  with  $0.5 \leq c \leq 0.7$  is caused by the decrease in  $(\sigma_{\text{ion}}/\sigma)$ . For the  $\text{Cu}_2\text{Se}$ -rich mixtures, the value of  $\sigma_{\text{el}}$  is much larger than that of  $\sigma_{\text{ion}}$ . Therefore, the value of  $S$  on the  $\text{Cu}_2\text{Se}$ -rich side depends mainly on the first term on the right-hand side of eq.(3). Assuming that  $Q_{\text{ion}}/eT + (kT/en_i)(\partial n_i/\partial T) + \alpha_1 = S_{\text{II}}$  is  $412 \mu\text{V/K}$  at  $1423 \text{ K}$ , the values of  $(\sigma_{\text{ion}}/\sigma)S_{\text{II}} = S_{\text{ion}}$  at  $1423 \text{ K}$  are  $46 \mu\text{V/K}$  and  $14 \mu\text{V/K}$  for molten  $(\text{CuCl})_{0.3}(\text{Cu}_2\text{Se})_{0.7}$  and liquid  $\text{Cu}_2\text{Se}$ , respectively. According to the assumption, we obtained the values of  $S_{\text{ion}}$  of molten mixtures as shown in Fig.4. The value of  $(\sigma_{\text{el}}/\sigma)(-Q_{\text{el}}/eT)$  of eq.(3) on the  $\text{Cu}_2\text{Se}$ -rich side can also be obtained from this process.

Enderby and Barnes have suggested that the  $\sigma_{\text{el}}$  and  $(-Q_{\text{el}}/eT)$  of molten mixtures can be analyzed by the Kubo-Greenwood formula [2]. Therefore we apply the energy dependent conductivity with a conductivity gap  $\Delta E = E_c - E_v$  to eqs.(2) and (4). The energy dependent conductivity,  $\sigma(E)$ , is given by [2],

$$\sigma(E) = a_c(E - E_c), \quad (E \geq E_c) \quad (5)$$

$$a_v(E_v - E), \quad (E_v \geq E) \quad (6)$$

where  $a_c$  and  $a_v$  are the coefficients of the energy dependent conductivity for electron and hole states, respectively. The equations of (5) and (6) are schematically shown in Fig.5. Considering the values of

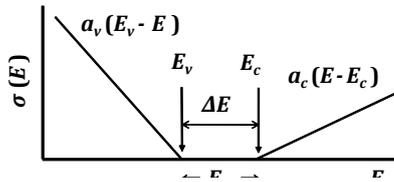


Fig.5 Electronic model of  $\sigma(E)$  proposed by Enderby and Barnes [2].

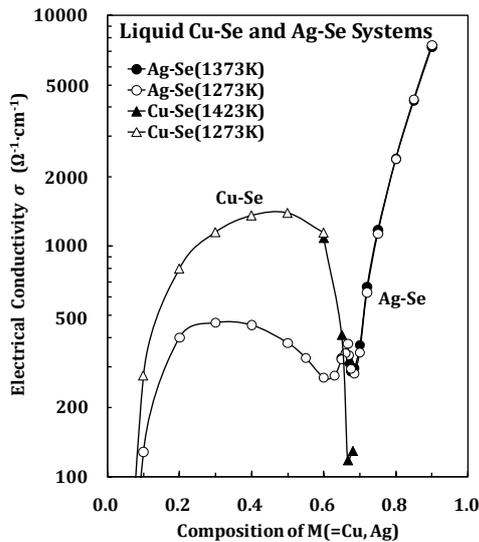


Fig.6 A comparison between the composition dependence of  $\sigma$  for liquid Cu-Se and Ag-Se systems. The solid lines are guide for eye. The values of  $\sigma$  for liquid Cu-Se and Ag-Se were obtained from refs.2, 9 and 15.

conductivity and thermoelectric power, we assume that the conductivity gap  $\Delta E$  is  $0.25 \text{ eV}$  for liquid  $\text{Cu}_2\text{Se}$ . In the case of  $\Delta E = (E_c - E_v) \gg kT$ , Enderby and Barnes have found special equations putting eqs.(5) and (6) in the first term on the right-hand side of eq.(2) and the first term on the right-hand side of eq.(3) as follows:[2]

$$\sigma(T) = kT \exp(-\Delta E/2kT) \{ a_c \exp(E_F/kT) + a_v \exp(-E_F/kT) \}, \quad (7)$$

$$S(T) = (k/e) \left[ \frac{a_v - a_c \exp(2E_F/kT)}{a_v + a_c \exp(2E_F/kT)} \right] \times \left\{ \left( \frac{\Delta E}{2kT} + 2 \right) + E_F/kT \right\}, \quad (8)$$

where the origin for  $E_F$  is taken as the center of the conductivity gap. For the liquid  $\text{Cu}_2\text{Se}$ , we estimated the  $a_c$  and  $a_v$  from the values of  $\sigma_{\text{el}}$  and  $S_{\text{el}}$  by eqs.(7) and (8). The values of  $a_c$  and  $a_v$  obtained in this way are  $930$  and  $2700 (\Omega \cdot \text{cm} \cdot \text{eV})^{-1}$ , respectively.

The large value of  $a_v$  for liquid  $\text{Cu}_2\text{Se}$  would be closely related to the large density of valence states which originates from the hybridization between the d states of Cu and the p states of Se. It is interesting that the electrical conductivity of liquid Cu-Se alloy is much larger than that of liquid Ag-Se in the wide range of 20-65 at% M (=Cu, Ag) as shown in Fig. 6 [2, 9, 15]. It suggests that the large density of valence states due to the p-d hybridization just below  $E_F$  yields a relatively large conductivity of liquid  $\text{Cu}_{1-c}\text{Se}_c$  with  $0.8 \geq c \geq 0.35$ . For liquid  $\text{Cu}_2\text{Se}$ ,  $E_F$  moves in the center of conductivity gap. As a result, a relatively small conductivity of liquid  $\text{Cu}_2\text{Se}$  corresponds to the electronic model with the conductivity gap of  $0.25 \text{ eV}$ .

It is well known that liquid  $\text{Ag}_2\text{Se}$  is zero-gap liquid semiconductor [2]. Under the condition  $\Delta E = 0 \text{ eV}$ , the  $a_c$  and  $a_v$  estimated for liquid  $\text{Ag}_2\text{Se}$  are  $4000$  and  $2450 (\Omega \cdot \text{cm} \cdot \text{eV})^{-1}$ , respectively. The large value of  $a_c$  originates from the large conductivity of liquid  $\text{Ag}_2\text{Se}$ . Liquid Ag-Se alloys have a large conductivity and a positive temperature coefficient of  $\sigma$  in the range 65-68 at% Ag. This unusual behavior is supported by measurements of

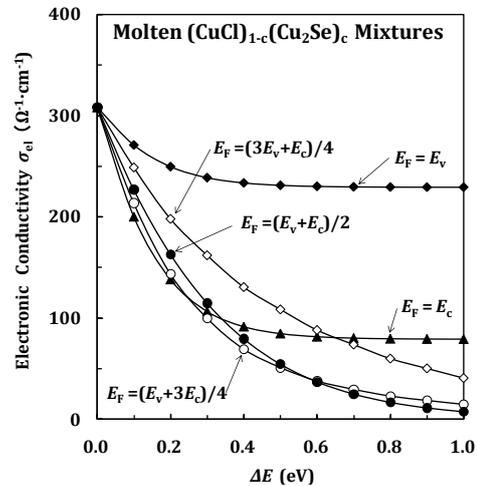


Fig.7 Dependence of electronic conductivity,  $\sigma_{\text{el}}$ , on  $\Delta E$  at the various positions of  $E_F$ . The solid lines are guide for eye.

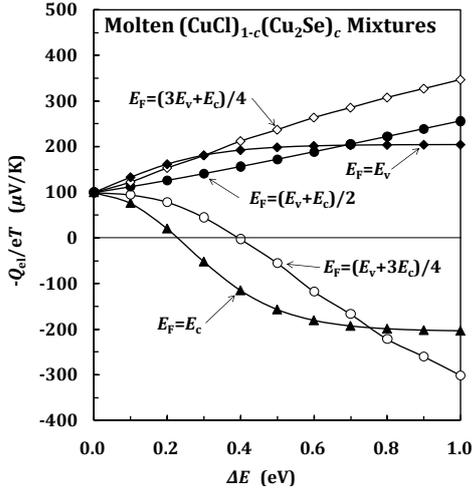


Fig.8 Dependence of thermoelectric power,  $(-Q_{el}/eT)$ , on  $\Delta E$  at the various positions of  $E_F$ . The solid lines are guide for eye.

the Hall mobility which are also found to be unusually high compared to other liquid semiconductors. The conductivity of  $Ag_2Se$  is  $730 \Omega^{-1}\cdot cm^{-1}$  at the temperatures just below the melting point. If a more ordered  $Se^{2-}$  sub-structure in liquid  $Ag_2Se$  remains somewhat, liquid  $Ag_2Se$  may behave as super ionic conductors with large value of  $\sigma$  at the higher temperatures [1]. This feature also takes place in molten  $(AgCl)_{1-c}(Ag_2Se)_c$  with  $c \geq 0.6$ .

Assuming that  $a_c$  and  $a_v$  are constant on the  $Cu_2Se$ -rich side, we can estimate the  $\sigma_{el}$  and  $(-Q_{el}/eT)$  for the various values of  $\Delta E$ . Figure 7 shows the electronic conductivity as a function of  $\Delta E$  in the five cases where  $E_F$  is located in the range between  $E_c$  and  $E_v$ . In two cases  $E_F = E_v$  and  $E_F = E_c$ , the value of  $\sigma$  approaches to  $230 \Omega^{-1}\cdot cm^{-1}$  and  $80 \Omega^{-1}\cdot cm^{-1}$  estimated from  $\sigma = a_c kT \cdot \ln 2$  and  $\sigma = a_v kT \cdot \ln 2$  with increasing  $\Delta E$ , respectively [2]. In the three cases where  $E_F$  is located in the conductivity gap, the electronic conductivity decreases smoothly with increasing  $\Delta E$ . The decrease in the electronic conductivity obtained experimentally suggests that  $E_F$  is located in the conductivity gap.

Figure 8 shows the thermoelectric power due to the conduction electrons as a function of  $\Delta E$ . The values of  $(-Q_{el}/eT)$  increase with  $\Delta E$  for  $E_v < E_F \leq (E_c + E_v)/2$  and approaches to the constant value of  $205 \mu V/K$  for  $E_F = E_v$ . On the other hand, The  $(-Q_{el}/eT)$  decreases with  $\Delta E$  for  $E_c > E_F \geq (3E_c + E_v)/4$  and approaches to the constant value of  $-205 \mu V/K$  for  $E_F = E_c$ . The  $(-Q_{el}/eT)$  is very sensitive to the position of  $E_F$  in the conductivity gap.

As shown in Fig.9, we plot the set of  $\sigma_{el}$  and  $(-Q_{el}/eT)$  which corresponds to the values estimated from the same value of  $\Delta E$  at the same position of  $E_F$  in Figs.7 and 8. A set of  $\sigma_{el}$  and  $(-Q_{el}/eT)$  for  $\Delta E = 0.4 eV$  is  $(92 \Omega^{-1}\cdot cm^{-1}, -115 \mu V/K)$  at  $E_F = E_c$  and moves up with decreasing  $E_F$  in Fig.9. The dotted lines are visual guides for the variation of  $E_F$ . The dashed lines are visual guides for the variation of  $\Delta E$  under the analogous condition of  $E_F$  in the gap. The corresponding plots obtained experimentally are also shown in Fig.9. Using eqs.(2) and (3), the experimental values of  $\sigma_{el}$  and  $(-Q_{el}/eT)$  for molten mixtures with  $c \geq 0.5$

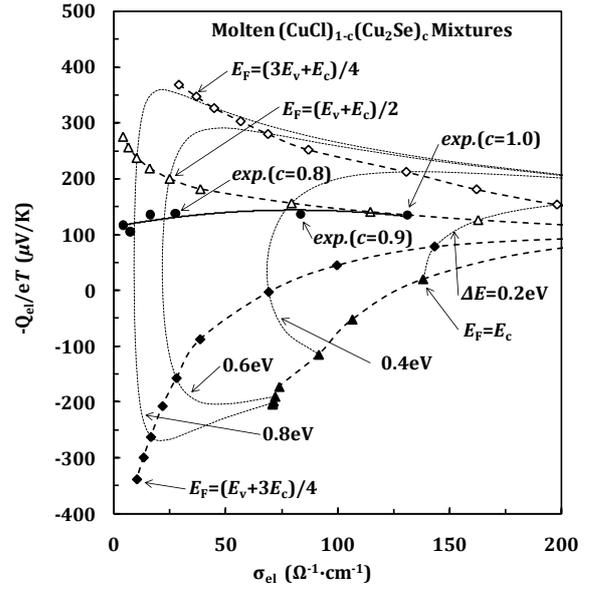


Fig.9 Plots of  $(-Q_{el}/eT)$  versus  $\sigma_{el}$  for various values of  $\Delta E$  at the various positions of  $E_F$ . The experimental values of  $\sigma_{el}$  and  $(-Q_{el}/eT)$  for molten mixtures with  $c \geq 0.5$  were estimated from the values of  $(\sigma - \sigma_{el})$  and  $(\sigma \sigma_{ion})(S - S_{ion})$ , respectively. The solid line is visual guides for these plots. The dotted lines are visual guides for the variation of  $E_F$  under the condition that  $\Delta E = \text{constant}$ . The dashed lines are visual guides for the variation of  $\Delta E$  under the analogous condition of  $E_F$  in the gap. The closed circles indicate the experimental values. The open diamonds, open triangles, closed diamonds and closed triangles indicate the values estimated under the condition that  $E_F = (3E_v + E_c)/4, (E_v + E_c)/2, (E_v + 3E_c)/4$  and  $E_c$ , respectively.

were obtained from the assumptions that  $\sigma_{ion} = 5.5 - 7.0 \Omega^{-1}\cdot cm^{-1}$  and  $S_{II} = 412 \mu V/K$ . The solid line is visual guides for their plots of  $(-Q_{el}/eT)$  versus  $\sigma_{el}$ . The composition dependence of  $\Delta E$  can be roughly obtained from the plots of  $(-Q_{el}/eT)$  versus  $\sigma_{el}$ . The plots indicate that the  $\Delta E$  increases gradually on the addition of  $CuCl$  to liquid  $Cu_2Se$ . The values of  $\Delta E$  were found to be about  $0.37 eV, 0.56 eV$  and  $0.68 eV$  for molten  $(CuCl)_{1-c}(Cu_2Se)_c$  with  $c = 0.9, 0.8$  and  $0.7$ , respectively. The position of  $E_F$  for molten  $(CuCl)_{1-c}(Cu_2Se)_c$  with  $c \geq 0.5$  is located near the centre of conductivity gap.

## 5 Conclusion

Liquid  $Cu_2Se$  is typical liquid semiconductors with a conductivity gap of  $0.25 eV$ . For molten  $CuCl-Cu_2Se$  mixtures, the value of  $\sigma$  decreases and the value of  $S$  increases steadily as the  $CuCl$  is added. The composition dependence of  $\sigma$  and  $S$  can be explained from the simplified model of energy dependent conductivity. According to this analysis, the conductivity gap of their mixtures increases gradually with the addition of  $CuCl$  to liquid  $Cu_2Se$  and the dominant transport process changes from electronic to ionic conduction. Molten  $(CuCl)_{0.3}(Cu_2Se)_{0.7}$  has a large conductivity gap of  $0.68 eV$ . In contrast to the  $AgCl-Ag_2Se$  system, the relatively smooth increase in their composition dependence of  $S$  is

observed in this region where the transition takes place.

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