Semiconducting Behavior in the Molten Tl–CuTe System

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Measurements of electrical conductivity, magnetic susceptibility and thermoelectric power of the liquid Tl–CuTe system were carried out over wide temperature and composition ranges. The composition dependences of the electronic properties investigated exhibit that there is a deep minimum in electrical conductivity, a sharp maximum in diamagnetic susceptibility and a rapid change in the sign of thermoelectric power around 50 mol% Tl, which are considerably similar to the case of the well-known compound-forming liquid system, Tl–Te. These experimental results suggest that the localization of valence electrons is very remarkable at the stoichiometric composition of CuTlTe in the present system. In fact, the $g$-factor at this composition calculated by the strong scattering model is lower than 1/3 which is often used as the limiting condition when electrons in disordered systems begin to be localized. Furthermore, it is also expected through the application of the pseudogap theory to observed values of the electrical conductivity and the thermoelectric power that the carrier band structure has a marked asymmetric form in the vicinity of 50 mol% Tl in this system.

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I. Introduction

It has been well-known that the electronic properties of liquid Te are in an intermediate state between the metal and the semiconductor. Most of Te-based liquid alloys have a wide miscible region and then the measurement of their electronic properties is possible over a wide range of composition. The observed concentration dependence of electronic properties of these liquid alloys often shows an anomalous behavior in the vicinity of the particular stoichiometric composition, such as minima of both electrical conductivity and electron susceptibility and an inverse in the sign of thermoelectric power. Several theories have vigorously been proposed to interpret these anomalous behavior. For example, the nearly free electron approximation (Enderby and Collings 1970), the semiconductor based model (Cutler 1971), the disorder-induced mobility gap model (Mott 1971), and the percolation model (Cohen and Jortner 1973). Recently the molecule association model which assumes the presence of some kind of stoichiometric compounds in the solution has been developed and successfully explained the anomalies of these electronic properties. However, the defect of this model is that the microscopic structure and the life-time of compounds present in the solution have not been made clear up to now.

In any way, it may be reasonably considered at present that non-metallic chemical bondings between neighboring atoms are formed around a particular composition where an anomaly in electronic properties occurs. Therefore, in order to derive an answer for the validity of the theoretical models it seems very noteworthy to investigate experimentally whether the chemical bonding is covalent or rather ionic, how the valence electrons in the solution are localized and how the chemical bonding affects the local atomic arrangement.

The present authors have measured electronic properties of the liquid pseudo-binary system, Ag–TlTe, and found that the system exhibits the same anomalies at the composition of AgTlTe as mentioned above. From the chemical similarity between Ag and Cu, it can

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probably be expected that a similar behavior in electronic properties also appears at the composition of CuTlTe in the liquid Tl-CuTe system.

The object of this paper is to describe new data on the electrical conductivity, the thermoelectric power and the magnetic susceptibility in the liquid Tl-CuTe system and to discuss the bonding nature and the electron localization around the stoichiometric composition of CuTlTe with the help of current transport schemes for liquid semiconductors.

II. Experimental Procedures

The purities of starting materials used were better than 99.999%. CuTe was prepared in advance from both components. All the samples were made by carefully sealing required amounts of both Tl and CuTe in an evacuated quartz tube and by mixing thoroughly in the molten state. The heating time of more than 144 ks (40 h) was adopted to achieve a good homogeneity for the sample.

The electrical conductivity was measured through the direct current four-probe technique. The apparatus consists mainly of a highly purified alumina crucible and a fused quartz conductivity cell with tungsten electrodes. The crucible containing the liquid sample can be moved up and down in order to stir the alloy and to remove absorbed gases. A calibration factor for the conductivity cell was determined by measuring purified mercury before each measurement.

The measurement of the magnetic susceptibility was made by the usual Faraday method. A horizontal force on a sample exerted by the magnetic field was measured by a Curie-Chenevean type tortion balance (Shimadzu Co., Ltd.). Hence the effects due to perpendicular forces acting on the sample such as the buoyancy and the thermomolecular effect could be neglected in the balance system. The temperature was determined by PR thermocouple fixed near the sample position. The sample sealed in an evacuated quartz cell was heated in a PID-SCR controlled silicon carbide electric furnace. The magnetic force was calibrated relative to both Mohr's salt and purified titanium at room temperature.

To measure the thermoelectric power, the temperature gradient between two potential electrodes inserted into both ends of a quartz cell filled with the liquid sample was introduced by a supplementary heater placed near the hot end of the cell and by moving the main furnace. Thermovoltages of the sample were calibrated against molybdenum.

For both conductivity and thermoelectric power measurements high purity argon was used to stress the vapourization of the sample in the cell.

III. Experimental Results

Measurements of the electrical conductivity, \(\sigma\), the atom magnetic susceptibility, \(\chi\), and the thermoelectric power, \(S\), for liquid CuTe have already been made by Dancy \(^8\) and Okada et al. \(^9\). The numerical comparison between the

![Fig. 1 Logarithmic curve of electrical conductivity, \(\sigma\), against reciprocal temperature in the liquid Tl-CuTe system.](image)
present and the previous results is impossible because previous data are graphically plotted. However, it appears that the present results at 1073 K of $\sigma = 1.98 \times 10^5 \text{S/m}$, $\chi = -9.8 \times 10^{-11} \text{m}^3/\text{mol}$ and $S = +43 \mu \text{V/K}$ are all in rough agreement with respective data reported by previous investigators within experimental errors. In addition, temperature dependences of these electronic properties are quite similar among the present and the previous results.

Observed results for $\sigma$ and $\chi$ in the liquid Tl–CuTe system are described in Figs. 1 and 2 as a function of temperature, respectively. The slope of logarithmic plots of $\sigma$ versus $1/T$ increases abruptly when the concentration of Tl approaches 50 mol% which corresponds to the stoichiometric composition of CuTlTe; in other words, the activation energy of electronic conduction in the system tends to be much larger in the concentrated range. The temperature change of $\chi$ for alloys near 50 mol% Tl is somewhat larger at high temperatures, suggesting that the system is rather covalent than ionic. Isotherms of $\sigma$ and $\chi$ in the liquid Tl–CuTe system are respectively given in Figs. 3 and 4 against mole per cent of Tl. We find a pronounced minimum of $\sigma$ and a
The transport theory based on the diffusive motion of electrons has often been applied for liquid chalcogenides with the range of $2.0 \times 10^4 \leq \sigma \leq 2.5 \times 10^5$ S/m. According to the theory, the electrical conductivity, $\sigma$, relates to the density of electron states near the Fermi level, $N(E_F)$, as

$$\sigma = A[N(E_F)]^2 (11).$$

The magnetic susceptibility, $\chi$, can also be expressed in the metallic approximation,

$$\chi = \chi_{\text{dia}} + B_{\mu_B^2} N(E_F)^{1/2},$$

where $\chi_{\text{dia}}$ is the total diamagnetic contribution in the system. Combining eq. (1) with eq. (2), the following relation holds between $\sigma$ and $\chi$:

$$\chi = \chi_{\text{dia}} + B_{\mu_B^2} \sigma^{1/2} / A^{1/2}. (3)$$

This equation related to the delocalized electron scheme cannot be applied satisfactorily for alloys near 50 mol% Tl with $\sigma \leq 2.0 \times 10^4$ S/m. We should have much fuller information on the energy dependence of $\sigma(E)$ and $N(E)$ around $E_F$ for these alloys in order to find a more accurate relationship between $\sigma$ and $\chi$. However, since the information is not available, an attempt was made to discuss the semiconductive properties of the whole system using eq. (3) as a first approximation.

The result for the application of eq. (3) to the present data is shown in Fig. 7. The slope
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of lines formed by the data points of above 50 mol% Tl alloys is less steep than that from the data of CuTe rich alloys, which means that the former alloys have either an increasing constant $A$ or a decreasing constant $B$. A larger value of $A$ near 50 mol% Tl suggests that $N(E_F)$ falls deeply when the concentration of Tl approaches 50 mol%, because $\Gamma_D$ gives a sharp minimum at this composition.

The constant $B$ involves two contributions in the metallic model, the spin paramagnetism and the orbital diamagnetism of valence electrons in the system. Therefore, a decrease in the value of $B$ corresponds to an increase in the orbital diamagnetism. In any way, an abrupt decrease in the slope of lines for alloys in the vicinity of 50 mol% Tl in Fig. 7 is considered to indicate that the localization of valence electrons strongly occurs around the composition of CuT1Te in the liquid Tl-CuTe system.

The value of $X_{dia}$ per atom of liquid CuT1Te determined by the extrapolation of the line for 50 mol% Tl alloy to the $\sigma^{1/2}=0$ axis can be estimated at $-4.21 \times 10^{-10}$ m³/mol per atom. Assuming that CuT1Te is a simple ionic liquid, the diamagnetic contribution, $[X_{dia}]$, in the alloy is assumed as follows:

$$[X_{dia}] = \frac{1}{3} [ \chi_0(\text{Cu}^+) + \chi_0(\text{Tl}^+) + \chi_0(\text{Te}^{2-}) ] .$$  (4)

Here, the diamagnetic susceptibilities, $\chi_0$, of Cu$^+$, Tl$^+$ and Te$^{2-}$ ions have been tabulated by Selwood$^{(13)}$. The difference between experimental $X_{dia}$ and calculated $[X_{dia}]$ is $\sim -6.9 \times 10^{-11}$ m³/mol, which is larger than that for liquid AgT1Te, $-3.8 \times 10^{-11}$ m³/mol, reported previously$^{(7)}$. This indicates that the bonding nature of liquid CuT1Te is less ionic than that of liquid AgT1Te which is considered as a partially ionic liquid.

The value of $g$ denoting the ratio of real density of states of electrons at the Fermi level to the free electron value has been well employed as a measure of the electron localization in liquid chalcogenides. The constant $A$ of eq. (1) can be rewritten through the weak scattering approximation,

$$A \simeq \frac{\pi^2}{3} \frac{e^2 \cdot h^2}{m^2 \cdot a} ,$$

where $a$ is the mean free path of electrons which can be assumed to be an interatomic distance in the present chalcogenide system being nearly 0.3 nm. Then, for highly electronic conductors the following relation can be derived between $\sigma$ and the ratio of electron density of states, $g$:

$$\sigma = \frac{e^2 \cdot n^{2/3} \cdot a}{(3\pi^2)^{1/3} \cdot h} \cdot g^{2(e)} .$$  (5)

where $n$ is the electron concentration per unit volume in the solution.

The composition dependence of $g$ calculated using the experimental values of $\sigma$ at 973 K in the liquid Tl-CuTe system is shown in Fig. 8. Density data at 973 K necessary for the determination of $n$ were $1.07 \times 10^4$ kg/m³ for liquid Tl and $6.31 \times 10^2$ kg/m³ for liquid CuTe, respectively. Densities of respective compositions were obtained by the compositional average from respective components using both values.

The composition dependence of $g$ in the Tl-CuTe system exhibits a deep minimum at 50 mol% Tl. As expected from observed results of $\sigma$ the minimum value of $g$ at the composition...
of CuTlTe is slightly larger than that of liquid AgTlTe, $g \approx 0.13$ at 973 K, previously determined in the same method\(^7\). However, since $g \approx 1/3$ is well known as the critical condition that the state density of electrons is deep enough to begin the electron localization\(^4\), it can be pointed out that the electrons in the Tl-CuTe system are considerably bound in the vicinity of 50 mol% Tl.

When the state density of electrons is negligibly small or the states are strongly localized, that is to say, the pseudogap appears, the conduction occurs through carriers excited into the extended state. According to the pseudogap theory, $\sigma$ relates to $S$ as below, assuming the equivalence of activation energies of $\sigma$ and $S$,

$$\ln \sigma = \ln \sigma_0 - \frac{|e|}{k_B} |S| + A_0^{(16)}.$$  (6)

In this equation a constant $A_0$ depending on the scattering mechanism can be approximated to be unity. Figure 9 shows the relation of log $\sigma$ vs $|S|$ for four concentrated alloys in the liquid Tl-CuTe system, where data on 49 and 50 mol% Tl alloys are not contained because of a marked anomaly of $S$ against temperature as seen in Fig. 5. Both activation energies of $\sigma$ and $S$ generally disagree due to such effects as the hopping transport in the localized states and the coexistence of carrier electrons and holes. The line slopes from data on 40 and 45 mol% Tl alloys are smaller than the ideal value in eq. (6), $|e|/(2.303)k_B$, denoted by the thin line. This suggests that the metallic contribution cannot be neglected for the electronic conduction. On the other hand, the data points from more than 50 mol% Tl alloys fall upon the lines with a much larger slope than the theoretical value. Considering the magnitude of $\sigma_0$ expected from the extrapolation of the line to $|S|=0$ axis, it seems that these alloys do not lie in the range commonly associated with the hopping process. These lines are too steep to apply any carrier model with a symmetric density of states. Therefore, we are compelled to consider that the band structure of carriers in the alloys is remarkably asymmetric. However, in the present time there is no evidence that the carrier density of states in the neighborhood of the Fermi level has an asymmetric form in these alloys. It is desired that detailed measurements of the band structure in spectroscopic and optical fields are carried out for the liquid Tl-CuTe system in the near future.

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