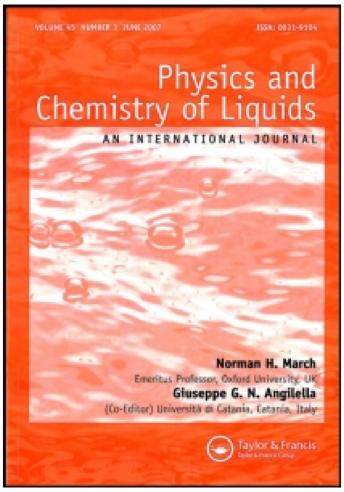

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Electrical Conductivity and Magnetic Susceptibility of Liquid $Tl_2(Te_xSe_{1-x})$ Mixtures

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The electrical conductivity σ and the magnetic susceptibility χ of liquid $Tl_2(Te_xSe_{1-x})$ mixtures have been measured up to 900°C. The concentration dependence of magnetic susceptibility due to the conduction electrons, χ_e, is considerably small in the intermediate concentration range at low temperature and χ_e changes continuously at high temperature.

1 INTRODUCTION

The X-ray diffraction pattern for liquid Tl_2Te[1] shows simply damped oscillation and the thermodynamic data[2] indicate that concentration fluctuation $S_{cc}(0)$ is extremely small in liquid Tl_2Te. These pieces of evidence encourage us to believe that the atomic arrangement of liquid Tl_2Te is quite isotropic like those of some molten salts.[3,4] Although there are no available X-ray diffraction and thermodynamic data for liquid Tl_2Se, it may be expected that the atomic arrangement of liquid Tl_2Se is quite isotropic as well as that of liquid Tl_2Te. Recent X-ray photoemission measurement[4,5] reveals that there exists stronger ionicity in solid Tl_2Se than that in solid Tl_2Te. By replacing Se atoms in liquid Tl_2Se with Te atoms, the nature of the bonding between Tl and atoms surrounding the Tl is expected to change. As a result, the electronic band structure may change. The magnetic susceptibility provides rather direct information about the density of states at the Fermi level, $N(E_F)$, so its measurement in liquid $Tl_2(Te_xSe_{1-x})$ mixtures is of some importance. Comparison of the data for the magnetic susceptibility χ and the electrical conductivity σ provides further information about the electronic structure for these mixtures.

In this paper, we report the results of σ and χ of liquid $Tl_2(Te_xSe_{1-x})$ mixtures.

2 EXPERIMENTAL PROCEDURE

It is well known that the liquid-liquid two-phase region exists near the stoichiometric composition Tl_2Se and Tl_2Te in liquid Tl–Se[6] and Tl–Te[7] systems, respectively. Therefore, in order to make sure whether or not the mixtures are homogeneous, we have used a multi-electrode cell which was designed for the detection of the two-phase region.[7] The cell was made of Pyrex glass with six or eight tungsten electrodes. Homogeneous mixtures were obtained by mixing the specimen in the rocking furnace around 600°C. The temperature was measured by an alumel:chromel thermocouple.

Magnetic susceptibility measurements were carried out by the usual Faraday method. The specimen was sealed in a quartz tube under vacuum. In order to minimize the diamagnetic contribution from the quartz-cell and -holder, we have made their wall thickness as thin as possible. The specimen cell is 5 mm in diameter and 25 mm in axial length. The magnetic field strength was 5730 G with a pole piece gap 60 mm and the product of the magnetic field and its gradient, $H(\partial H/\partial x)$, was $1.92 \times 10^6\ G^2/cm$. As a standard, Mohr's salt $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ was used.

The concentration of the specimen was determined by weighing Te, Se (both 99.999% purities) and Tl (99.99% purity). The experimental error in the temperature was less than 1.0% while the error in the conductivity was less than 2%. The error in the susceptibility was no more than 1.0×10^{-6} emu/mole.

3 RESULTS AND DISCUSSIONS

In Figure 1, the results of σ are plotted as a function of reciprocal temperature for different liquid $Tl_2(Te_xSe_{1-x})$ mixtures. The temperature variations of σ for Tl_2Te and Tl_2Se agree with the results of Cutler[8] and of Nakamura and Shimoji,[9] respectively. It is noted that the plots of $\log \sigma - 1/T$ in these mixtures are accurately linear except near the melting points.

In Figure 2, the temperature coefficients of σ, $d \ln \sigma/d(1/k_BT)$, at 550°C are shown for the mixtures of $Tl_2(Te_xSe_{1-x})$. The temperature coefficient has the

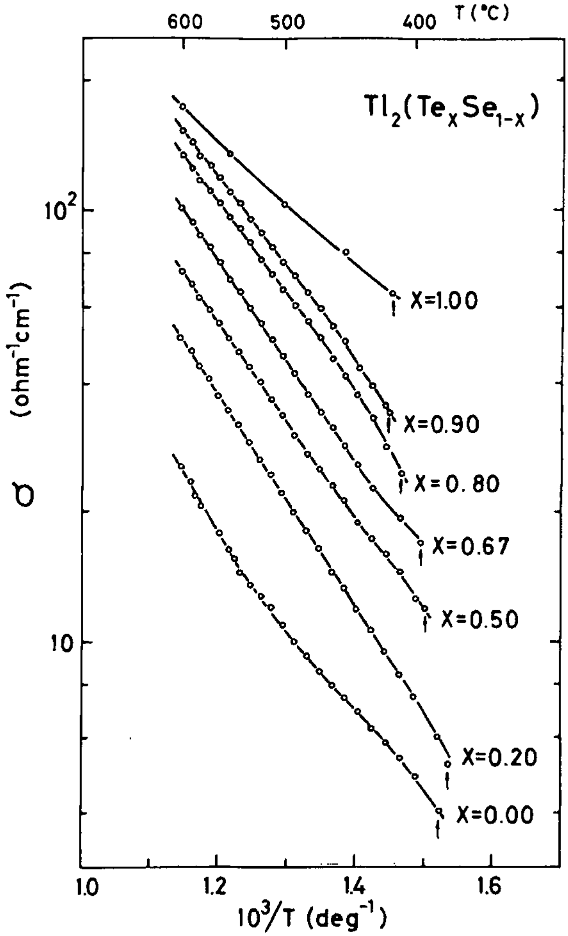

FIGURE 1 Logarithmic plot of conductivity as a function of reciprocal temperatures for liquid $Tl_2(Te_xSe_{1-x})$ mixtures. Arrows indicate the melting points of mixtures.

largest value for Tl_2Se. It decreases gradually with addition of Tl_2Te and drops sharply near Tl_2Te.

Figure 3 shows the concentration variations of σ at 500 and 600°C. As seen in this figure, σ increases considerably with a slight addition of Tl_2Te to Tl_2Se and by further increasing Tl_2Te concentration the rate of increase in σ becomes small. Above 50 mole % Tl_2Te σ again increases rapidly.

In Figure 4, the molar susceptibility χ_{tot} for various $Tl_2(Te_xSe_{1-x})$ mixtures is shown as a function of temperature. Values of χ_{tot} for 10, 30, 40 and 60 mole % Tl_2Te mixtures have been omitted from this figure for purposes of clarity. The present result of χ_{tot} for Tl_2Te agrees with the previous results by

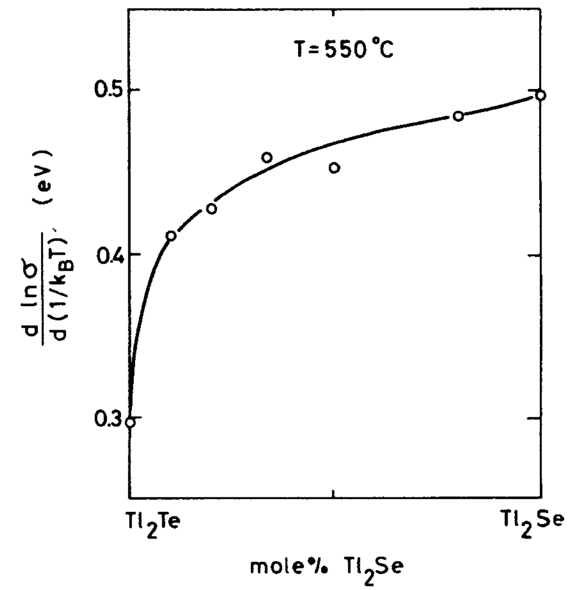

FIGURE 2 Temperature coefficients of conductivity, d ln $\sigma/d(1/k_BT)$, at 550°C for liquid $Tl_2(Te_xSe_{1-x})$ mixtures.

Uemura *et al.*,[10] by Tsuchiya *et al.*[11] and by Gardner and Cutler[12] within the experimental errors. For Tl_2Se the present result is in agreement with the result by Uemura *et al.*[10] within experimental error. The values of χ_{tot} are negative and increase with temperature in the whole concentration range.

The magnetic susceptibility χ_{tot} is given by

$$\chi_{tot} = \chi_i + \chi_e, \tag{1}$$

where χ_i is the ion core contribution and χ_e the contribution from the conduction electrons which is proportional to $N(E_F)$. According to the diffusive conduction model predicted by Mott,[13] σ is proportional to $\{N(E_F)\}^2$. Therefore, χ_{tot} should be a linear function of $\sigma^{1/2}$. Though the values of σ in these mixtures are relatively small[12] and do not cover wide temperature ranges,[14,15] we have attempted to plot χ_{tot} as a function of $\sigma^{1/2}$. Such plots are shown in Figure 5 for liquid $Tl_2(Te_xSe_{1-x})$ mixtures with $x = 0.2, 0.5$ and 0.8. As seen in this figure, the points all fall nicely around the straight lines. From these intercepts χ_i are obtained for the respective concentrations. Figure 6 shows the values of χ_i estimated from the plots χ_{tot} versus $\sigma^{1/2}$ for various concentrations of liquid $Tl_2(Te_xSe_{1-x})$ mixtures. These values of χ_i are in reasonable agreement with the calculated values of χ_i[16] by assuming that the ionic species in liquid $Tl_2(Te_xSe_{1-x})$ mixtures are Tl^+, Te^{2-} and Se^{2-}.

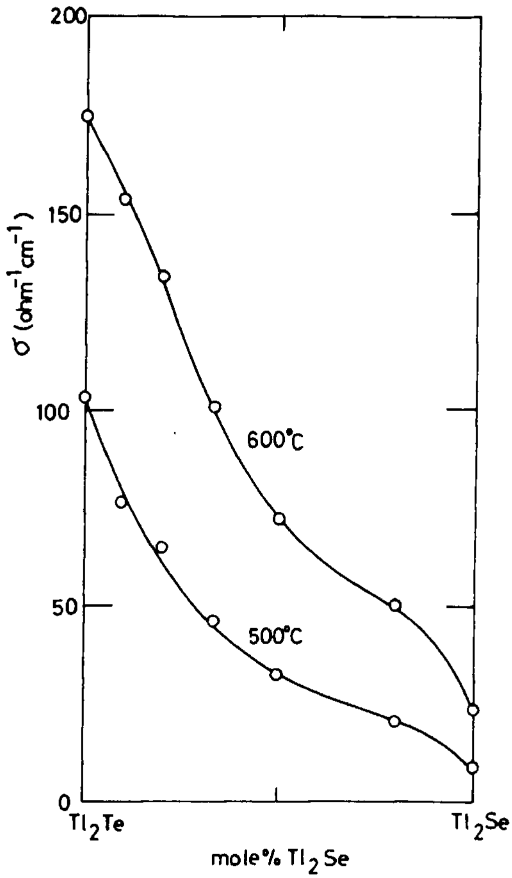

FIGURE 3 Concentration variations of conductivity at 500 and 600°C for liquid $Tl_2(Te_xSe_{1-x})$ mixtures.

Figure 7 shows χ_e estimated by subtracting χ_i from χ_{tot} for liquid $Tl_2(Te_xSe_{1-x})$ mixtures at different temperatures. It is found that χ_e has a positive sign and increases with increasing temperature. As seen in the figure, χ_e decreases rapidly with a slight replacement of Te atoms in liquid Tl_2Te by Se atoms and by further increasing Tl_2Se concentration the rate of decrease in χ_e becomes extremely small. Near Tl_2Se, χ_e decreases again. It should be emphasized that the region where the concentration change of χ_e is considerably small diminishes with increasing temperature. This region is indicated by the broken line in Figure 7.

The fact that σ and χ_e decrease largely by replacing Te in liquid Tl_2Te to Se atoms may be associated with a rapid destruction of the structure in liquid Tl_2Te. This structural change may cause the drastic increase of the temperature

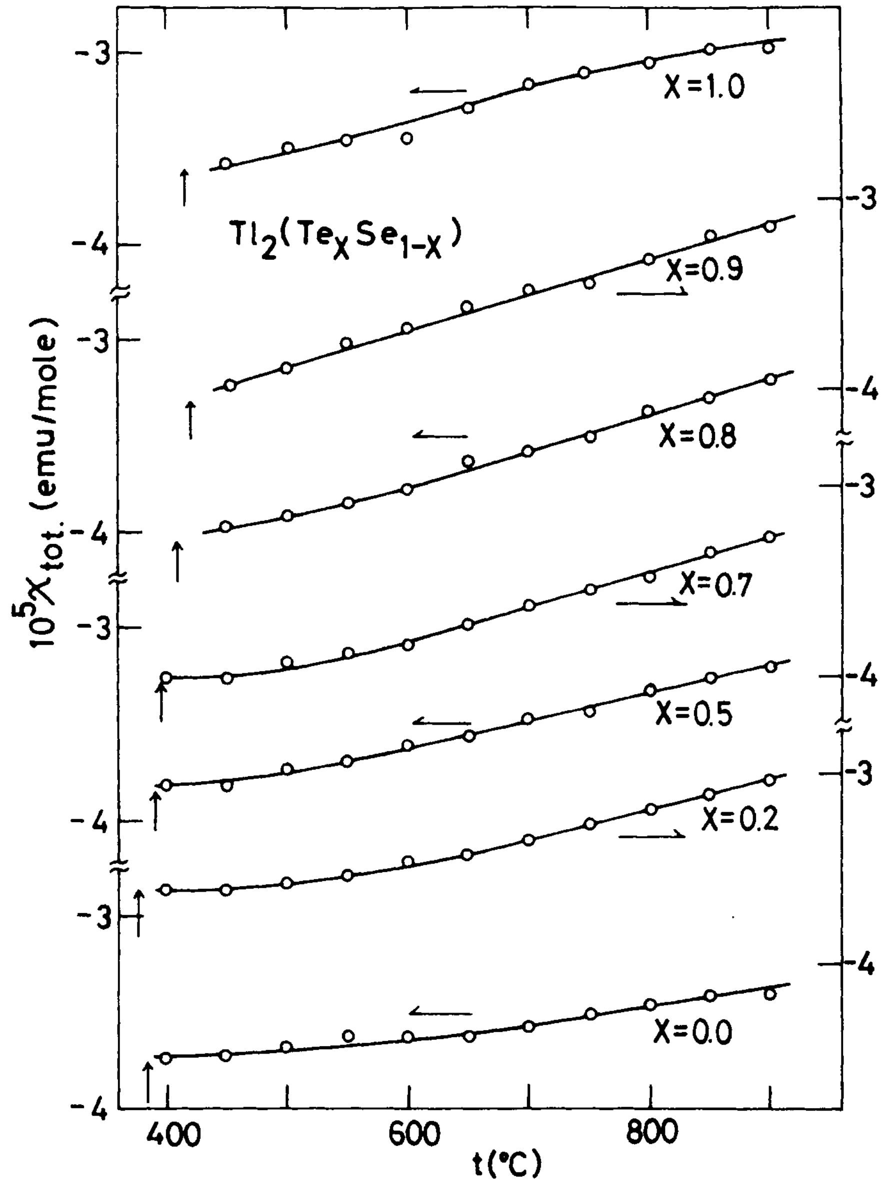

FIGURE 4 Temperature variations of molar susceptibility χ_{tot} for liquid $Tl_2(Te_xSe_{1-x})$ mixtures. Arrows (↑) indicate the melting points of mixtures. Note discontinuities in vertical scale.

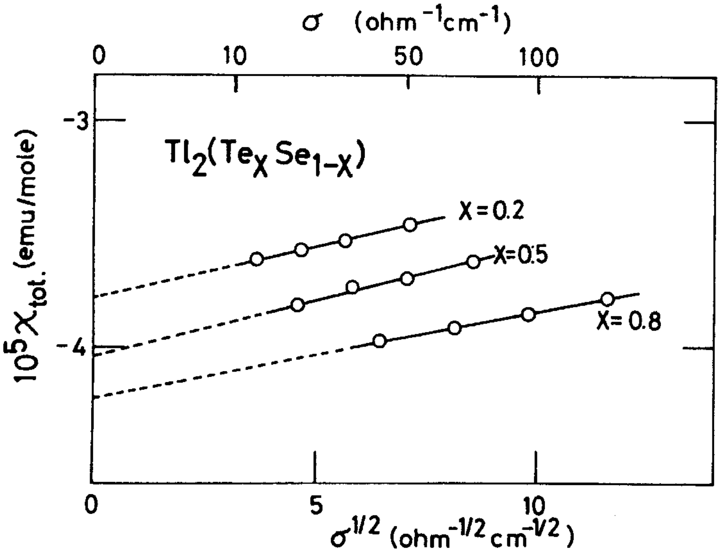

FIGURE 5 Molar susceptibility versus $\sigma^{1/2}$ for liquid $Tl_2(Te_xSe_{1-x})$ mixtures with $x = 0.2$, 0.5 and 0.8.

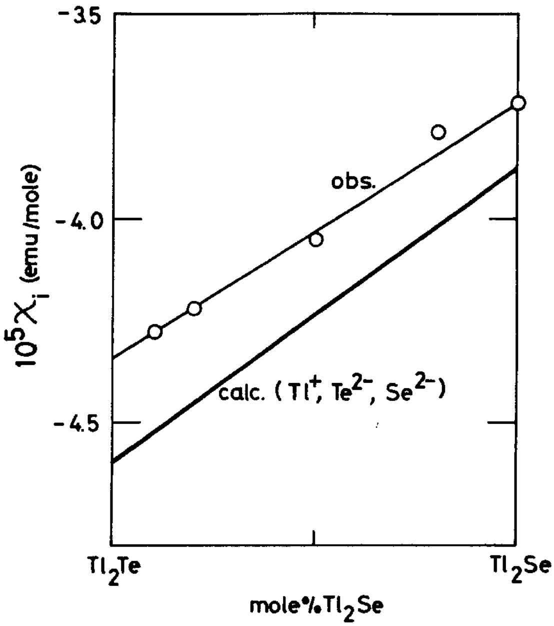

FIGURE 6 Ion core diamagnetisms χ_i of liquid $Tl_2(Te_xSe_{1-x})$ mixtures. Open circles denote the values obtained as the intercepts at $\sigma = 0$. Bold line indicates the calculated values of χ_i by assuming Tl^+, Te^{2-} and Se^{2-} ions in the liquid $Tl_2(Te_xSe_{1-x})$ mixture.

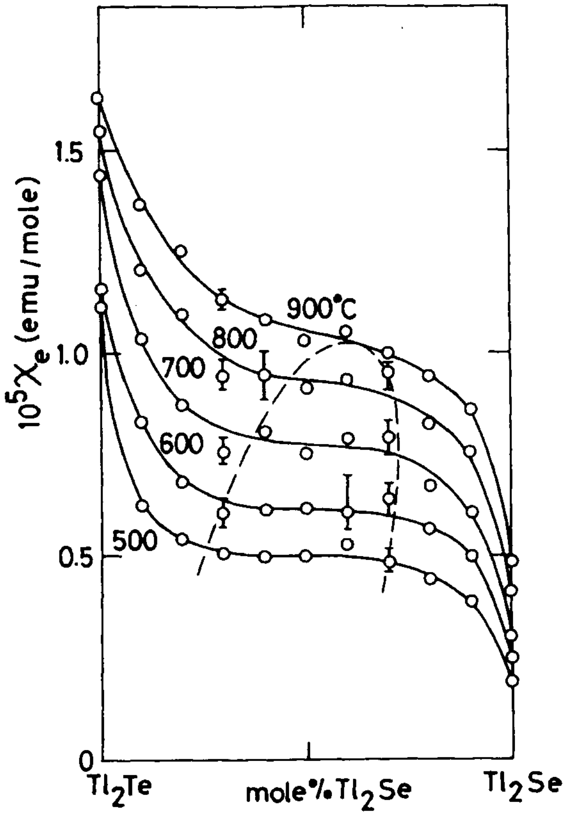

FIGURE 7 Electronic contribution to the susceptibility, χ_e for liquid $Tl_2(Te_xSe_{1-x})$ mixtures as a function of concentration at different temperatures. Broken line indicates the region where the χ_e remains nearly constant.

coefficient of σ, d ln $\sigma/d(1/k_BT)$, as shown in Figure 2. On the other hand, by replacing Se in liquid Tl_2Se to Te atom the value of d ln $\sigma/d(1/k_BT)$ changes slightly. This may be related to a gradual structural change in liquid Tl_2Se by the addition of Te, which may associate with the evidence that Tl_2Se has stronger ionicity than Tl_2Te.

Since χ_e is proportional to $N(E_F)$, the concentration variation of χ_e is considered to correspond to the change of $N(E_F)$. It is interesting that the change of $N(E_F)$ is small in the intermediate concentration range at low temperature and $N(E_F)$ changes continuously with concentration at high temperature. At the present stage, it is difficult to interpret this interesting behavior and we cannot exclude a possibility that this is associated with the presence of microscopic inhomogeneities in the concentration range inside the broken line. Measurements of NMR, X-ray diffraction and thermodynamic properties should be helpful for understanding the phenomenon.

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