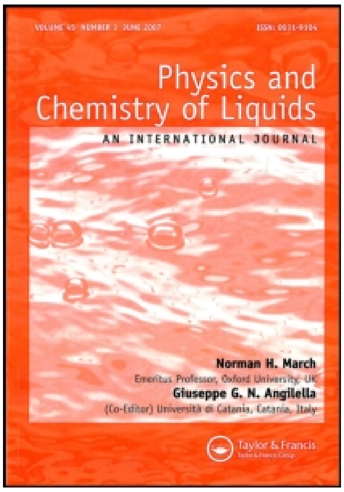

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The Magnetic Susceptibility of Liquid Thallium Chalcogenides

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The magnetic susceptibilities of liquid Tl-Te, Tl-Se and Tl-S systems have been measured at various compositions as a function of temperature. The difference of susceptibility between solid and liquid states at the melting point is quite small at the composition corresponding to Tl_2X (X = Te, Se and S). The diamagnetic susceptibility of these alloys in X rich region increases on melting, while that of Tl rich solutions decreases. The curve of isothermal susceptibility against concentration showed a diamagnetic maximum near the stoichiometric composition. These experimental results are discussed in the light of the bond orbital model for magnetic susceptibility.

1 INTRODUCTION

Liquid binary systems consisting of thallium and chalcogen elements are known to be typical semiconducting materials, electrical properties of which have been extensively examined.[1] At the composition of Tl_2X (X = Te, Se and S), the electrical conductivity for these systems has a deep minimum and the thermo-electric power changes its sign.[2–5]

Magnetic susceptibility can lead directly to an understanding of the electron localization for liquid semiconductors. Gardner and Cutler[6] have investigated the magnetic susceptibility of liquid Tl-Te system as a function of composition and temperature in detail, and have discussed on the validity of the conduction model proposed by Mott that the transport is governed by a diffusive motion of electrons in the extended state. Recently, Tsuchiya, *et al.*[7] have measured the magnetic susceptibilities of liquid alloys containing tellurium. They have reported that the anomalous behaviour of electronic properties around the composition Tl_2Te in the liquid Tl-Te system cannot be explained by the formation of solid-like chemical compound but by the activation process like in solid semiconductors.

The purpose of the present paper is to report the results of magnetic susceptibility measurement for liquid Tl-Te, Tl-Se and Tl-S systems and to discuss the difference of electronic properties appeared in these liquid semiconductors.

2 EXPERIMENTAL DETAILS

Purities of the elements used in this investigation were 99.999% for Tl, Te and Se, and 99.95% for S, respectively. The alloy of required composition was prepared by reacting both elements at 150°C above its liquidus temperature for 60 hr in a vacuum-sealed quartz cell (8 mm in inner diameter). The apparatus and experimental procedures for measurements of the magnetic susceptibility were identical to those described elsewhere.[8]

3 EXPERIMENTAL RESULTS

3.1 Tl-Te system

The magnetic susceptibility χ of liquid Tl_xTe_{1-x} with $x = 0.59$ to 0.70 is plotted in Figure 1 as a function of temperature. The experimental value of

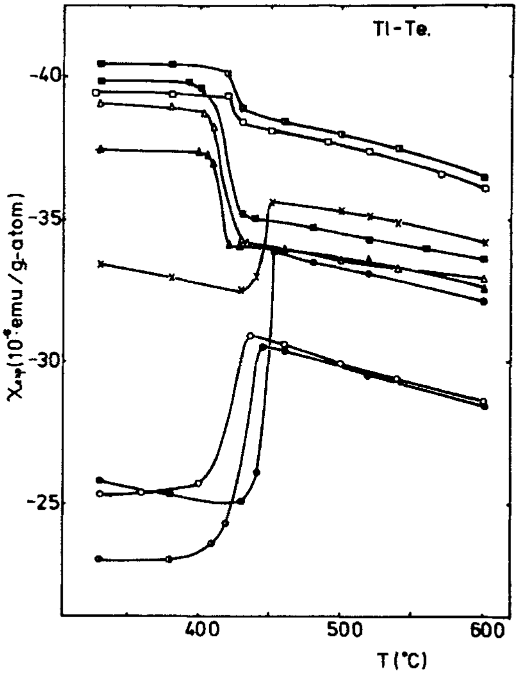

FIGURE 1 The temperature dependence of magnetic susceptibility for liquid Tl-Te alloys. -○-, 59 at%Tl; -◑-, 61 at%Tl; -●-, 63 at%Tl; -×-, 65 at%Tl; -□-, 66.6 at%Tl; -◧-, 67 at%Tl; -■-, 68 at%Tl; -△-, 69 at%Tl; -▲-, 70 at%Tl.

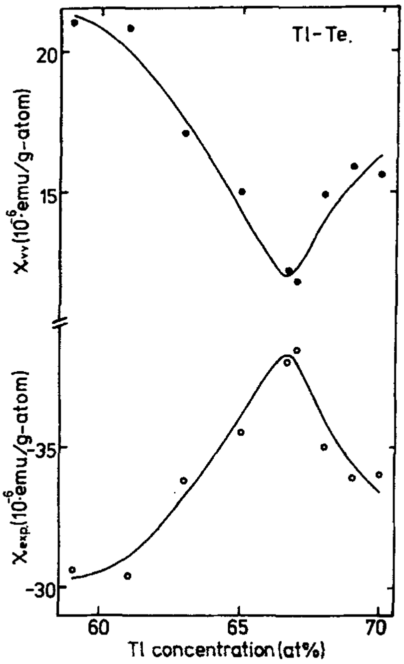

FIGURE 2 The composition dependence of magnetic susceptibility for liquid Tl-Te system at 460°C. -○-, experimental value; -●-, calculated one of Van Vleck paramagnetism.

χ at $x = 0.67$ at 500°C, -3.80×10^{-5} emu/g-atom is compared with -3.75×10^{-5} emu/g-atom by Tsuchiya *et al.*[7] and -3.54×10^{-5} emu/g-atom by Gardner and Cutler.[6] The present results are, on the whole, in good agreement with the previous data within experimental errors. The diamagnetic values of χ in the liquid state decrease gradually with increasing temperature. The diamagnetic susceptibility for $x \geq \frac{2}{3}$ decreases on melting, while that for $x < \frac{2}{3}$ increases. The change in χ at the melting point is considerably small at $x \simeq \frac{2}{3}$. These results are similar to those of liquid Tl-Se and Tl-S systems. Figure 2 shows the plots of isothermal susceptibility at 460°C against composition, The susceptibility isotherm has a sharp maximum of diamagnetism at $x \simeq \frac{2}{3}$ in the composition range covered in this investigation. Similar maximum has often been seen in various binary systems of liquid semiconductors.[8] At the same composition the electrical conductivity gives rise to a deep minimum and the thermo-electric power changes its sign.[3] It has been proposed that these anomalies in some electronic properties are derived by some kind of clusters formed in the liquid state, which are related to the compounds existing in the crystalline state.

However, Tsuchiya, *et al.*[7] have suggested that the semiconducting behaviour around the composition of Tl_2Te in the liquid Tl-Te system is not

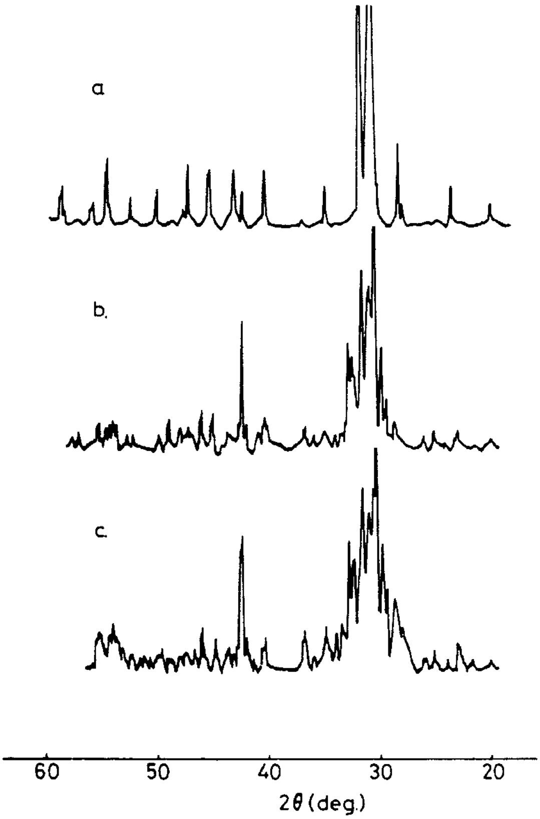

FIGURE 3 The X-ray diffraction patterns of powdered samples. (a) 63.0 at%Tl; (b) 66.6 at%Tl; (c) 70.0 at%Tl

due to the formation of solid-like compound. They also pointed out that the temperature dependence of its electronic properties is not caused by the dissociation of clusters but by activation process like in solid semiconductors. They gave as an important evidence for their argument that no solid intermetallic compound Tl_2Te exists in the Tl-Te system. Certainly, solid compound corresponding to Tl_2Te has not been reported in the conventional phase diagram of Tl-Te system.[9,10] However, it has not been clear at present whether this compound exists or not.

Figure 3 shows the X-ray diffraction patterns of powdered samples for 63.0, 66.6 and 70.0 at%Tl alloys. The diffraction pattern for 63.0 at%Tl agrees well with that of γ phase (Tl_5Te_3) confirmed by Bhan and Schubert[11] and Rabenau, *et al.*[12] If there is no compound in the Tl rich region above γ phase as reported until now, 66.6 at%Tl alloy ought to consist of a mixture of Tl rich γ phase and a very small amount of Tl phase. Therefore, the diffraction pattern of 66.6 at%Tl alloy is considered to be similar to that of 63.0 at%Tl alloy. As shown in the figure, however, the observed pattern differs considerably between two alloys in both view points of the intensity and the position of diffraction lines. The diffraction pattern of 70.0 at%Tl alloy agrees well with that of 66.6 at%Tl alloy. These results suggest that solid compound Tl_2Te may possibly exist in the Tl-Te system. In fact, the existence of Tl_2Te has ever been proposed by a few previous authors.[13,14] As shown in Figure 1, the difference of susceptibility between solid and liquid phases at melting point is the smallest at the composition corresponding to Tl_2Te. This also supports that liquid Tl_2Te possesses the local atomic order similar to that in the solid state.

3.2 Tl-Se and Tl-S systems

The temperature and composition dependences of χ for liquid Tl-Se and Tl-S systems given in Figures 4–7 are quite similar to those in the Tl-Te system. In these systems, the change of χ against temperature is remarkably small in the liquid phase. The difference of χ between solid and liquid states at the melting point is also small compared with the Tl-Te system.

Figure 8 shows the isothermal susceptibility at 400°C for liquid Tl-Se system over the composition range from pure Se to pure Tl. As shown in the figure, the curve of χ vs. composition has a distinct maximum of diamagnetism around Tl_2Se, although there are two solid compounds, TlSe and Tl_2Se_3

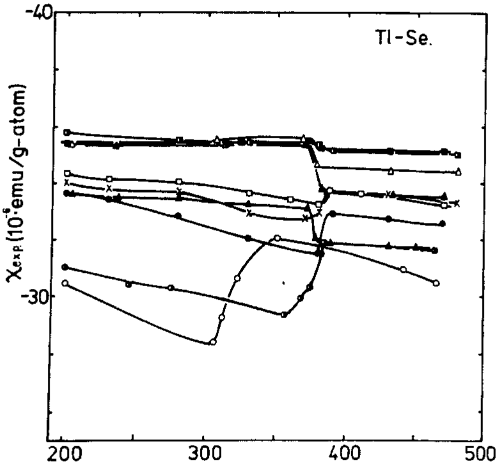

FIGURE 4 The temperature dependence of magnetic susceptibility for liquid Tl-Se system. -○-, 60 at%Tl; -◑-, 63.8 at%Tl; -●-, 65 at%Tl; -×-, 65.5 at%Tl; -□-, 66 at%Tl; -◨-, 66.5 at%Tl; -■-, 66.6 at%Tl; -△-, 67.3 at%Tl; -◭-, 67.6 at%Tl; -▲-, 67.9 at%Tl.

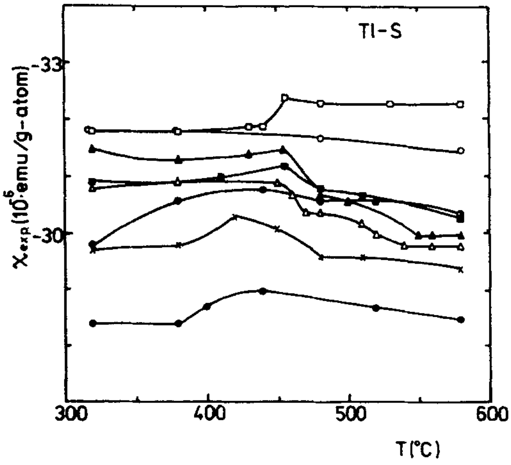

FIGURE 5 The temperature dependence of magnetic susceptibility for liquid Tl-S system. -○-, 57.9 at%Tl; -◐-, 61.9 at%Tl; -●-, 64 at%Tl; -×-, 66.1 at%Tl; -□-, 66.6 at%Tl; -■-, 67.5 at%Tl; -△-, 68 at%Tl; -▲-, 69 at%Tl.

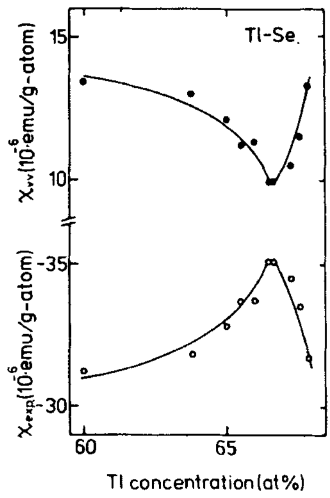

FIGURE 6 The composition dependence of magnetic susceptibility for liquid Tl-Se system at 400°C. -○-, experimental value; -●-, calculated one of Van Vleck paramagnetism.

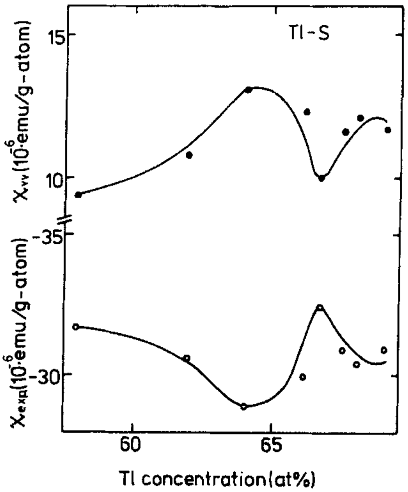

FIGURE 7 The composition dependence of magnetic susceptibility for liquid Tl-S system at 470°C. -O-, experimental value; -●-, calculated one of Van Vleck paramagnetism.

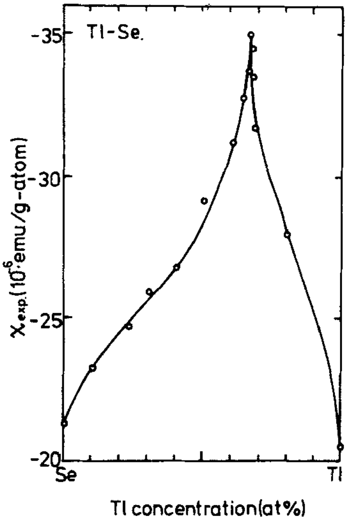

FIGURE 8 The plots of magnetic susceptibility versus composition in liquid Tl-Se system over the whole range of composition at 400°C.

besides Tl_2Se. A similar result on the position of diamagnetic maximum has been reported in the liquid Tl-Te system by Tsuchiya, *et al.*[7] This suggests that the bonding between unlike atoms becomes remarkably strong at Tl_2X in liquid binary systems containing thallium and chalcogen element.

4 DISCUSSION

The magnetic susceptibility for semiconductors is written approximately as a sum of three terms, core electron term χ_c, valence electron diamagnetic contribution χ_L, and Van Vleck paramagnetic term χ_{vv} using the bond orbital model. Chadi, *et al.*[15] have presented χ_L in the same Langevin form as χ_c;

$$\chi_L = -\left(\frac{Ne^2}{6mc^2}\right)\left(\frac{\gamma d}{2}\right)^2,$$

where, N is the electron density and d the interatomic distance, and γ is a scaling parameter which would be unity if the bond charge were concentrated at the atom sites. They find a value $\gamma = 1.13$ for silicon. Taking $\gamma = 1.13$, this term can be calculated when d is known. The radial distribution study of liquid Tl_2Te made by Waseda and Tamaki[16] gives $d = 3.20$ Å. This value is nearly close to 3.14 Å interpolated linearly using 3.24 Å for liquid Tl and 2.95 Å for liquid Te,[16] respectively. Therefore, it may be convenient to apply the Vegard's law on the determination of d in the liquid Tl-Te, Tl-Se and Tl-S systems. Using experimental values of χ and core electron susceptibilities of Tl^{+1}, Te^{+6}, Se^{+6}, and S^{+6} tabulated,[17] the isothermal χ_{vv} of three liquid systems are plotted against composition in Figures 2, 6 and 7. The data of d for liquid Se and S are quoted from Waseda, *et al.*[18] and Gingrich.[19] These curves show deep minima around the compositions, Tl_2Te, Tl_2Se and Tl_2S, that is to say, the electron localization occurs violently at these compositions. This is supported by various electronic properties such as electrical conductivity,[1] thermo electric power,[2] Hall coefficient[3] and so on.

The Van Vleck paramagnetic susceptibility χ_{vv} results from virtual magnetic dipole transitions between valence and conduction bands. It is proportional to an average interband magnetic dipole matrix element M and to the inverse of the average energy separation E_g of valence and conduction band states connected by the magnetic dipole operator. That is,

$$\chi_{vv} = \frac{(1-\alpha^2)|M|^2}{E_g},$$

where, α is ionicity.[20] The matrix element M which is sensitive to the symmetry of chemical bond seems to be nearly equal among Tl_2Te, Tl_2Se and

TABLE I

The Van Vleck paramagnetic contribution χ_{vv}, the electrical conductivity σ and the activation energy E for liquid Tl_2Te, Tl_2Se and Tl_2S.

	χ_{vv}($\times 10^{-6}$ emu/g-atom)	temp. (°C)	σ ($\Omega^{-1}cm^{-1}$)	temp. (°C)	E_a (eV)
Tl_2Te	12.3	460	82.0[a]	500	0.40[a]
Tl_2Se	9.8	400	10.5[a]	500	0.40[a]
Tl_2S	10.0	470	2.3[b]	448 (m.p.)	0.53[b]

[a] Ref. 3
[b] Ref. 4.

Tl_2S alloys. Table I shows χ_{vv} of these liquid alloys, together with their electrical conductivities and activation energies for conduction. The magnitude of χ_{vv} in Table I suggests that the magnetic band gap increases according to the order of Tl_2Se, Tl_2S and Tl_2Te although their ionicities are taken into consideration. On the other hand, the activation energy of electrical conductivity for liquid Tl_2S related to the thermal band gap is apparently larger than that for liquid Tl_2Se. This is inconsistent with the result given by the present work. The contradiction between magnetic susceptibility and electrical conductivity investigations may disappear if transport in liquid Tl_2S occurs in the localized states, since the conductivity in this case has rather large activation energy due to hopping. Whereas, it has been pointed out from the results of electron transport phenomena that the transport in liquid Tl_xSe_{1-x} ($x \lesssim \frac{2}{3}$) occurs in the mobility edge rather than in the localized states.[1] More exact informations on the bonding character between unlike atoms, however, will be needed to understand details of the transport in the liquid Tl_2S.

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