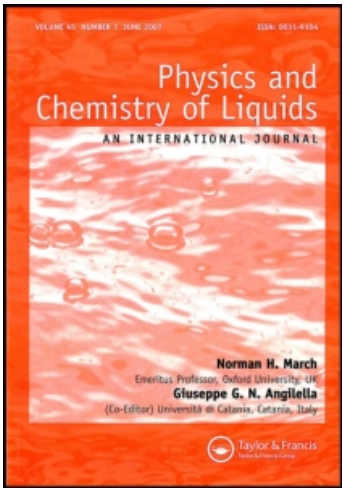

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Electrical Conductivity and Magnetic Susceptibility of the Molten Ag_2Te-In_2Te_3 System

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Both electrical conductivities and magnetic susceptibilities of the liquid Ag_2Te-In_2Te_3 system have been obtained as a function of temperature and composition from just above the melting point up to about 950°C. Small temperature coefficients of both quantities in pure Ag_2Te increase gradually with the addition of In_2Te_3 but above 71 mol%In_2Te_3, the temperature change becomes considerably smaller. Because of the above characteristics of these temperature dependences the composition change of these quantities along isotherm becomes larger with increase gradually with the addition of In_2Te_3 but above 71 mol%In_2Te_3, the temperature smooth curve near the composition of $AgInTe_2$(50%In_2Te_3), that is to say, no anomaly could be observed at this composition. From the relationship between the susceptibility and the square root of conductivity investigated using present data, it is suggested that the electronic density of states varies slightly near 75 mol%In_2Te_3 in the liquid Ag_2Tn-In_2Te_3 system. Using a scattering model for the electronic conduction, the critical temperature at which electron localization occurs is investigated over the whole range of composition under the assumption that 1, 3 and 2.5 electrons per atom contribute to the conduction in Ag, In and Te atoms, respectively.

1 INTRODUCTION

As is well known, liquid metal-Te systems are typical semiconducting systems and have been thoroughly investigated as regards their electronic properties.[1] In these liquid systems characteristic anomalies have been found in the plots of electron transport quantities against composition. For example sharp maxima have been observed in both the electrical resistivity and the diamagnetic susceptibility around the concentration at which there exists an intermetallic compound of the highest melting point in the solid state. These anomalies have often been discussed in terms of the formation of solid-like

clusters. The alloys which consist of two metal tellurides also have several intermediate phases in the solid state, such as $AgInTe_2$ in the Ag_2Te-In_2Te_3 system.[2] From the experimental results of electronic properties for liquid binary systems which include Te atom as one of the components, it is expected that an anomaly as seen in liquid Te alloys will be found around the stoichiometric composition of $AgInTe_2$ in the liquid pseudo-binary Ag_2Te-In_2Te_3 system.

Until recently the liquid Ag_2Te-In_2Te_3 system has been less well examined and few reliable data on the electronic properties have been reported. We have measured the electrical conductivity and the magnetic susceptibility of this liquid system over the whole range of composition in order to see how these electronic properties vary with composition. Further, we have discussed the composition dependence of electron localization using the experimental results.

2 EXPERIMENTAL

The purity of Ag, In and Te metals was better in each case than four nines grade. The specimens of required composition were prepared by reacting constituent elements thoroughly in the molten state in a quartz cell which is sealed in vacuum.

The electrical conductivity measurement was made with a four-terminal technique using tungsten electrodes and a fused quartz resistivity cell. The magnetic susceptibility was measured by the Faraday method with a torsion balance. The details of both measurements were identical to those described previously on the conductivity[3] and on the susceptibility,[4] respectively.

3 EXPERIMENTAL RESULTS

The measurement of electrical conductivity was made over the temperature range from 700°C to about 900°C. Temperature dependences of the conductivity for the liquid Ag_2Te-In_2Te_3 system are shown in Figure 1. As pointed out in the figure the conductivity can be plotted linearly versus temperature instead of the Arrhenius type plots in the temperature range covered in this work except for low temperatures. It is known about liquid In_2Te_3 that electrons bound owing to the compound-forming properties become delocalized rapidly with increasing temperature.[5,6] Reflecting this behaviour of electrons in In_2Te_3, the temperature coefficient of conductivity is considerably larger at the In_2Te_3 rich side of this system. On the other hand, it becomes rather smaller at the opposite side. A slight temperature

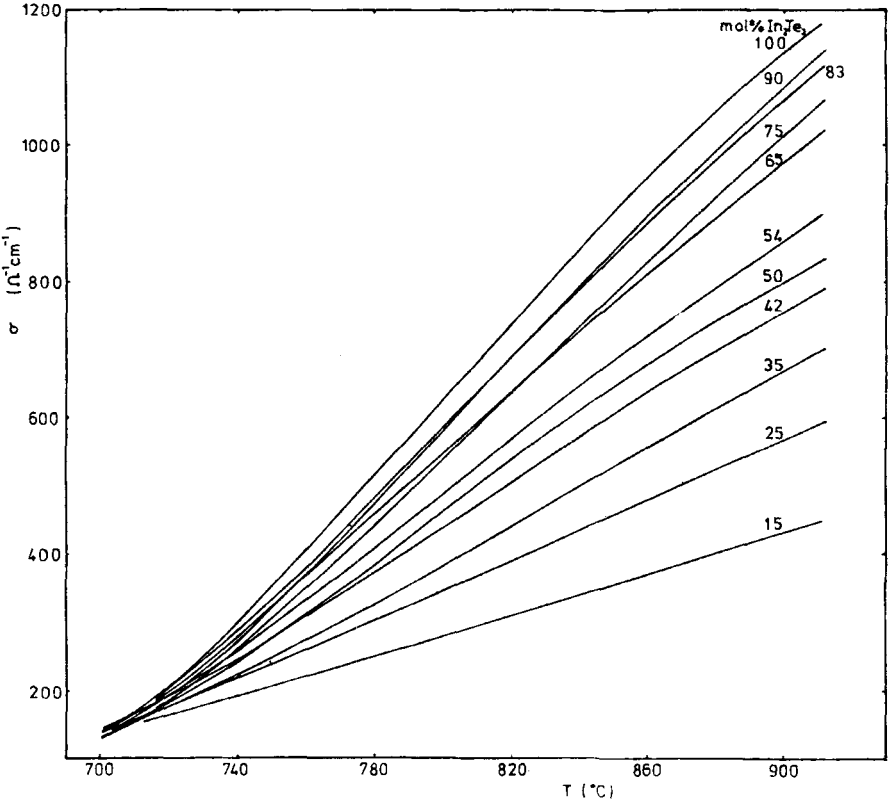

FIGURE 1 Electrical conductivity for liquid Ag_2Te-In_2Te_3 alloys.

dependence of the conductivity has been observed in several ionic liquid semiconductors such as Tl_2X(X: S, Se and Te).[7,8] Therefore, a gentle slope of the conductivity vs. temperature curve in the Ag_2Te rich alloys seems to indicate that the bond between Ag and Te atoms is more ionic than that between In and Te atoms. Figure 2 represents the relation between the temperature derivatives of conductivity and composition using data of 800° to 850°C. The temperature derivative increases gradually with increasing In_2Te_3 content and around 71 mol%In_2Te_3 the rate of increase becomes slow.

Curves of the electrical conductivity along an isotherm are shown in Figure 3, which display smooth forms versus concentration. No anomaly appears near the composition of $AgInTe_2$(50 mol%In_2Te_3) where a stable solid phase of chalocopyrite structure exists.[2] The composition dependence in the conductivity is relatively small at 740°C but considerably larger at 900°C.

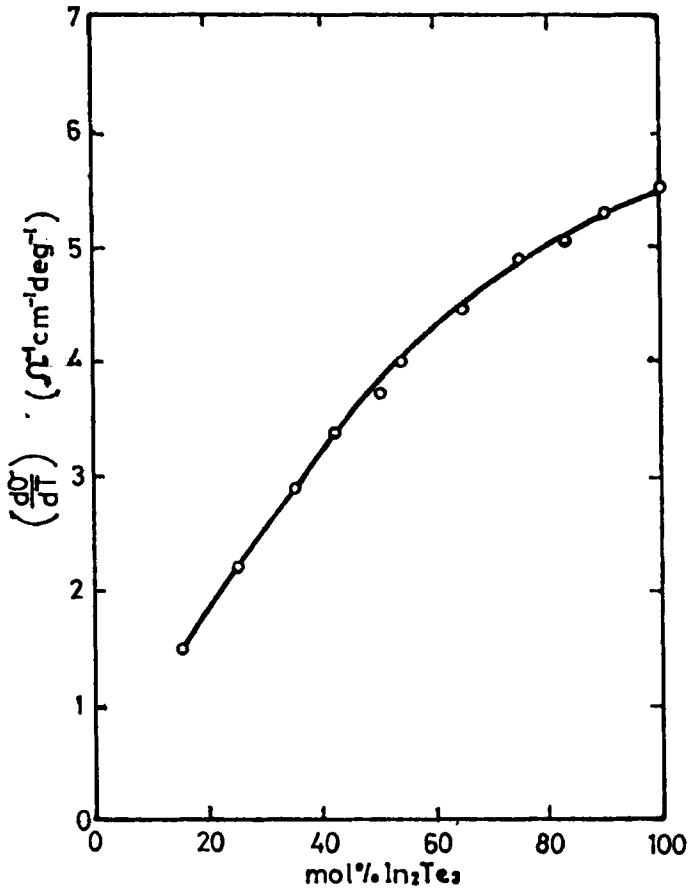

FIGURE 2 Composition dependence of the temperature derivative of conductivity.

In Figure 4, the magnetic susceptibility per *g*-atom for liquid Ag_2Te-In_2Te_3 alloys is plotted versus temperature. The difference of magnetic susceptibility at the melting point between solid and liquid phases, which remains severe in the concentration region from In_2Te_3 to $AgInTe_2$, becomes considerably smaller with descreasing In_2Te_3 content on the Ag_2Te side. The behaviour of the temperature derivative of susceptibility against composition resembles closely the case of the conductivity, that is to say, it increases gradually with increasing In_2Te_3 content at the Ag_2Te side and above 71 mol%In_2Te_3 it increases only a little.

A large diamagnetic susceptibility for liquid Ag_2Te decreases with the addition of In_2Te_3 as shown in Figure 5. The decrease in this diamagnetism

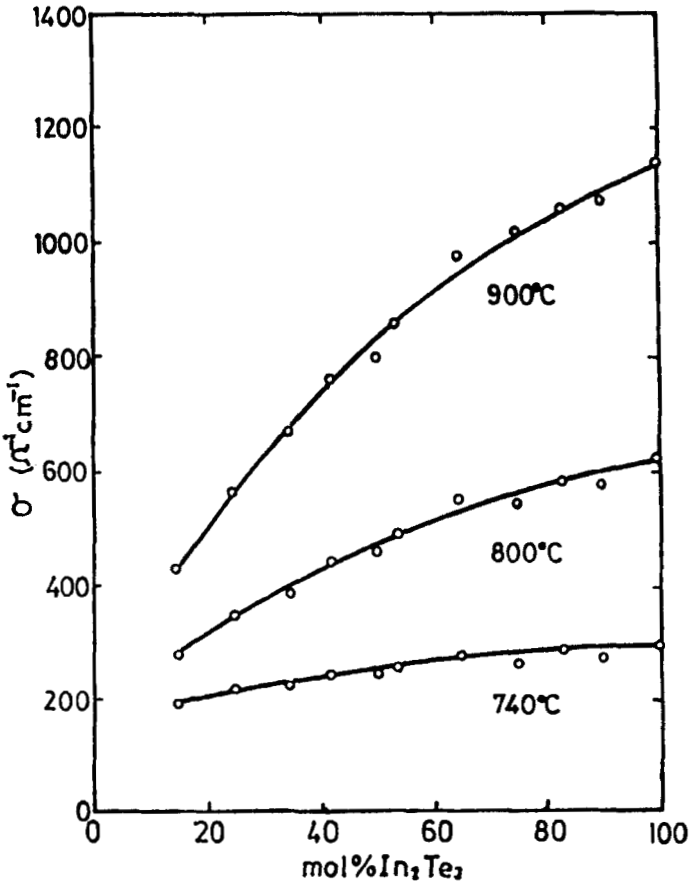

FIGURE 3 Composition dependence of the electrical conductivity.

along the composition of In_2Te_3 is considerable at high temperature, as also in the case of conductivity shown in Figure 3.

4 DISCUSSION

In spite of the existence of stable $AgInTe_2$ phase in the solid state the curves in Figure 5 shows a smooth form over the whole range of composition and no anomaly in the electronic properties appears around 50 mol%In_2Te_3 in the liquid state of Ag_2Te-In_2Te_3 system. Therefore, it may possibly suggest that the property of both Ag-Te and In-Te bonds in the liquid $AgInTe_2$

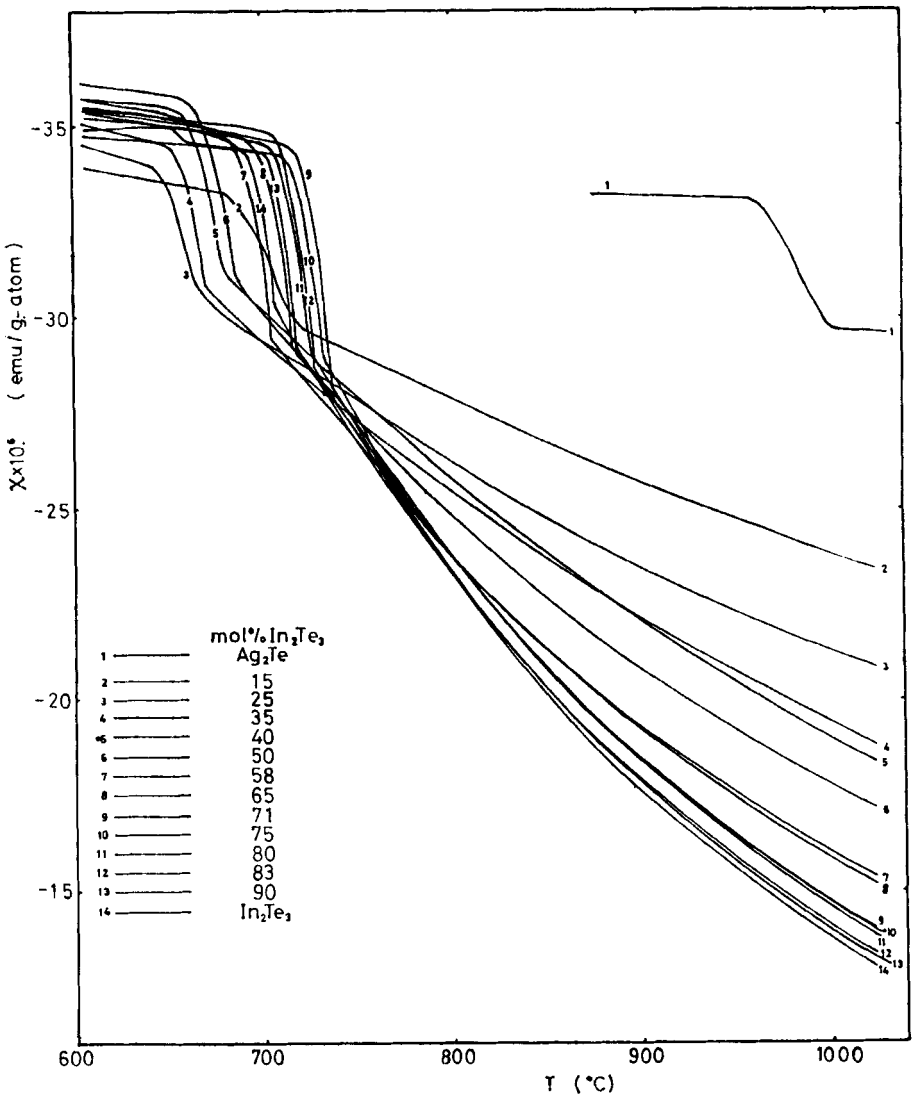

FIGURE 4 Magnetic susceptibility for the liquid Ag_2Te-In_2Te_3 system.

differs little from that in pure Ag_2Te and In_2Te_3, because electronic properties of liquid chalcogenides strongly depend upon the bonding character between unlike atoms. In fact, one of the authors has confirmed by the neutron diffraction experiment that the liquid phase of $(I_b)(III_b)(VI_b)_2$ type compounds does not have a short-range atomic arrangement as in the chalcopyrite structure.[9]

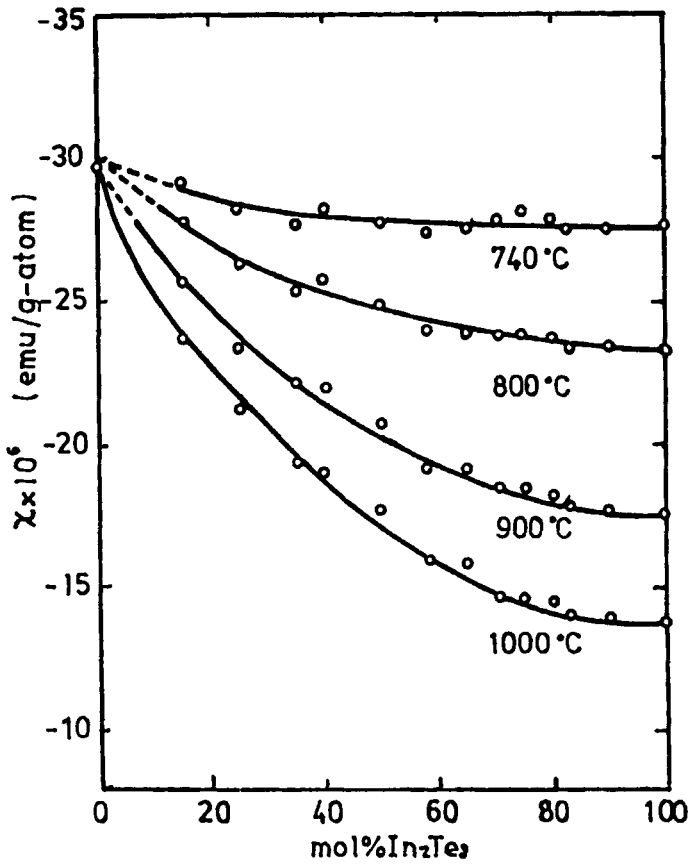

FIGURE 5 Composition dependence of the magnetic susceptibility for liquid Ag_2Te-In_2Te_3 alloys.

According to the bond orbital model, the magnetic susceptibility is given as a sum of three terms; the diamagnetic contributions of ion cores χ_{core}, valence electrons χ_L and the Van Vleck paramagnetism χ_{VV}. For example, the susceptibility per g-atom χ_A of $AgInTe_2$ can be written in the following equation (zero overlap model).[10]

$$\chi_A = \chi_{core}^{Ag^{1+}} + \chi_{core}^{In^{3+}} + 2\chi_{core}^{Te^{6+}} - \text{const.} \times (d^2 + d'^2) + \text{const.} \times \left\{ \frac{2(1-\alpha_p^2)}{E_+ - E_-} + \frac{2(1-\alpha_p'^2)}{E'_+ - E'_-} + \frac{(1+\alpha'_p)(1-\alpha_p)}{E_+ - E'_-} + \frac{(1+\alpha'_p)(1-\alpha'_p)}{E'_+ - E_-} \right\} \quad (1)$$

(prime: In-Te bond)

where, d, α_p and $E_\pm$ are the internuclear distance, polarity and the bonding($-$) and antibonding($+$) energy levels for the respective bonds. The various terms in Eq. (1) are calculated here as the following procedure.

1) χ_{core} is tabulated by Selwood.[11]

2) χ_L which depends on d is approximated in the same manner as mentioned in our previous paper.[12]

3) α_p necessary for determining last four terms is given using the approximate relation with the ionicity $f_i = 1 - (1 - \alpha_p)^{3/2}$.

Ionicities of the bonding Ag-Te and In-Te in $AgInTe_2$ are taken from the table of Bernard.[13] Two important energy differences $E_+ - E_-$ and $E'_+ - E'_-$ are determined using experimental values of the susceptibility of both pure liquids Ag_2Te and In_2Te_3 when it can be assumed that the character of Ag-Te and In-Te bonds remains unchanged on mixing. Other two energy differences $E_+ - E'_-$ and $E'_+ - E_-$ which belong to the correction terms are determined using energy parameters of the solid state listed in the table of Lines and Waszczak,[10] because the difference of these quantities between solid and liquid states can be neglected. The calculated results are compared with the observed susceptibilities of liquid $AgInTe_2$ in Table I in order to see

TABLE I

The calculated susceptibility of liquid $AgInTe_2$ by the bond orbital model with the observed values

	$-\chi_A \times 10^6$ (emu/g-atom)	
T(°C)	calc.	obs.
700	34.9	30.2
750	33.5	27.4
800	32.3	24.9
850	31.4	22.7
900	30.6	20.8
1000	29.3	17.8

whether the above assumption about the bonding character is valid. As the melting point of Ag_2Te 959°C is rather high the magnetic susceptibility for pure Ag_2Te at temperatures (except 1000°C) used in Table I is obtained extrapolating the measured value of Ag_2Te in the liquid region. The agreement between the observed and the calculated values is reasonable at 700°C. The discrepancy of both values, however, grows with increasing temperature. The character of Ag-Te bond is different, although in the solid state, between

$AgInTe_2$ and Ag_2Te phases. This bond is significantly covalent in the chalcopyrite type $AgInTe_2$; on the other hand it is slightly ionic in the monoclinic Ag_2Te, for example, the bond distance 2.79 Å in the chalcopyrite structure[2] is shorter than the corresponding value 2.95 Å (average) in the monoclinic crystal.[14] As shown in Table I, the temperature change of experimental values is quite large compared with that of calculated ones. Further, various experimental data investigated recently on the liquid semiconductors have indicated that electronic properties in covalentic compound-forming liquids give a violent temperature dependence because such compounds in the liquid state thermally dissociate into separate constituent atoms.[7,8] Consequently, it may be considered that the covalency of Ag-Te bond in the chalcopyrite structure of $AgInTe_2$ still remains to some extent in the liquid state.

The electrical conductivity of liquid alloys investigated in the present work is comparable to, or larger than, the critical value derived in the Mott criterion for electron localization except for the data near the melting point and at high Ag_2Te region. It is considered, therefore, that it is more suitable for the discussion of electronic properties of this system to utilize a diffusion regime of the electron conduction than a thermal hopping model for the localized electrons. In a diffusion regime[1] the conductivity σ is proportional to the square of the electron density of states at the Fermi level $[N(E)]_F$. Since the electron susceptibility is proportional to $[N(E)]_F$ in this regime, the following relation can be derived:

$$\chi = \chi_d + \text{const.} \times \sigma^{1/2} \tag{2}$$

where χ_d is the diamagnetic susceptibility mainly by ion core electrons. In the present work, it is rather difficult to judge exactly whether the data points at each concentration fall on a straight line because of some uncertainties in the experimental errors. The linear relation between χ and $\sigma^{1/2}$ in Figure 6, however, gives some information on the electron states of the liquid Ag_2Te-In_2Te_3 system. The slope of straight lines in Figure 6 decreases gently with increasing In_2Te_3 content but in the region from 75 mol%In_2Te_3 to In_2Te_3 it changes little. If χ_d term remains unchanged against temperature, the slope of the straight line corresponds to the constant in Eq. (2). In the diffusion regime the constant depends mainly on the electronic density of states.[1] It is considered, therefore, that change in the electronic density of states arises around 75 mol%In_2Te_3 when adding Ag_2Te to liquid In_2Te_3. The similar result can be observed in the curves for the temperature derivative of conductivity vs. composition as shown in Figure 2. Thus anomaly in the electronic density of states is considered to arise from the partial change of character of Ag-Te bond from covalent to ionic around this composition.

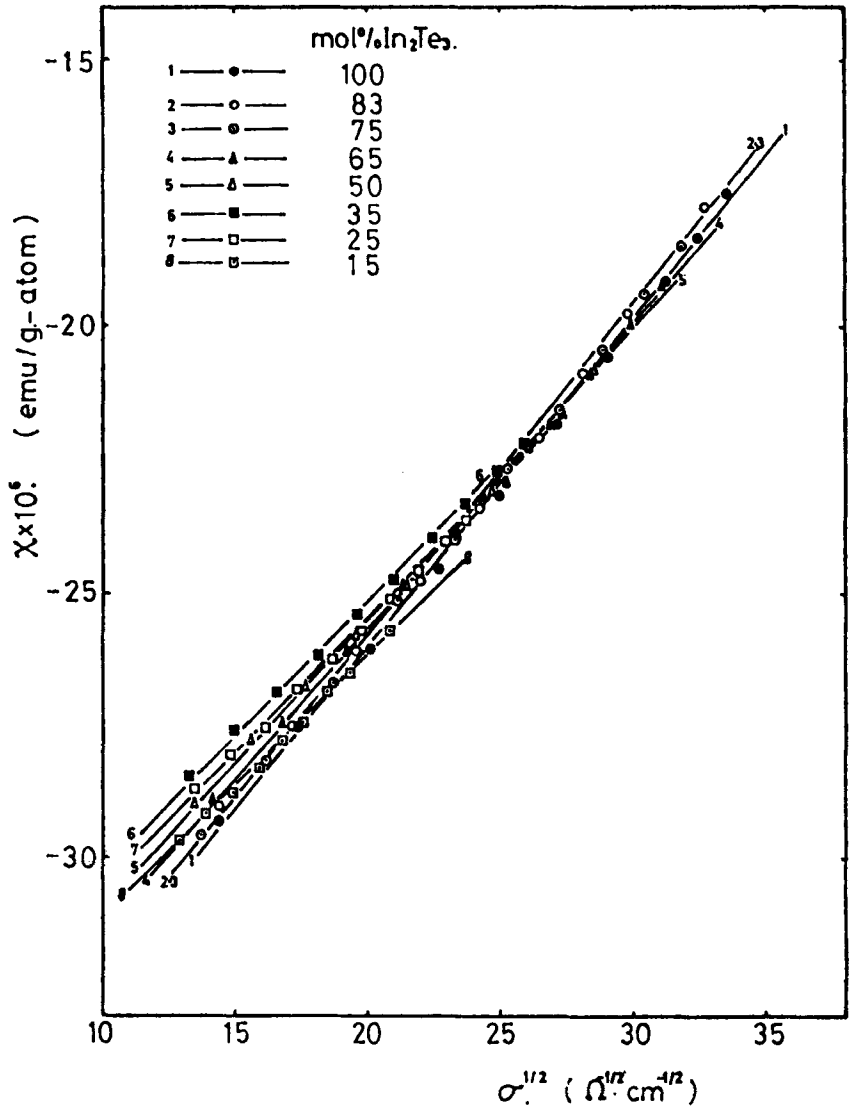

FIGURE 6 Relation between the magnetic susceptibility and the square root of electrical conductivity for liquid Ag_2Te-In_2Te_3 alloys.

It is of interest to estimate the degree of electron localization using electrical conductivity data. Assuming that electron states are not localized at the Fermi level, a strong scattering scheme for the conductivity can be used by writing

$$\sigma \simeq \frac{e^2 k_F^2 d g^2}{3\pi^2 \hbar} \tag{3}$$

where k_F is the wave vector at the Fermi level and d the average interatomic distance corresponding to the minimum of the electron mean-free path.[15] g denotes the ratio of the density of states at the Fermi level to that of the

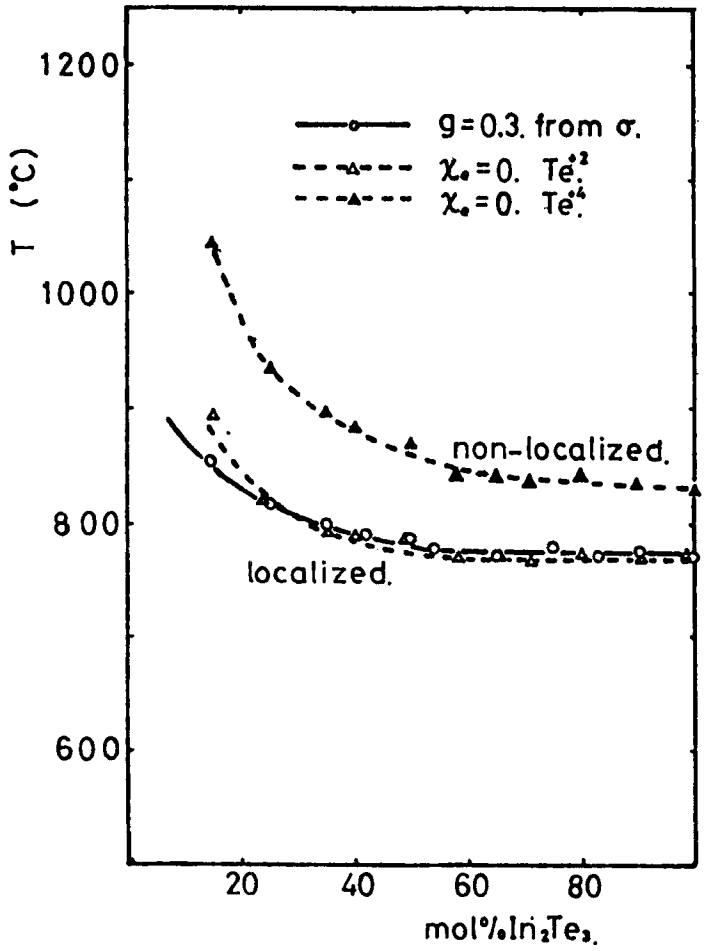

FIGURE 7 The phase diagram of liquid Ag_2Te-In_2Te_3 system for the electron localization.

free electron regime. We take 0.3 as the limiting value of g-factor in the strong scattering regime on the basis of the theoretical estimation of the Mott criterion for electron localization. Using the conductivity data the temperature at which we find $g \simeq 0.3$ can be determined.

The temperature-concentration diagram for the liquid Ag_2Te-In_2Te_3 system thus obtained is shown in Figure 6. To calculate Eq. (3) we take 2.5 electrons per atom as the number of conduction electrons in Te atom as reported for liquid Te.[16] Little change of the critical temperature can be found in Figure 7 for the alloys from In_2Te_3 to $AgInTe_2$. This temperature, however, increases in the Ag_2Te-rich concentration range. Another criterion for electron localization has been reported using magnetic susceptibility data. Tsuchiya *et al.*[6] have proposed the temperature at which the electronic susceptibility falls to zero as the localization temperature. To obtain the electronic susceptibility, the ion susceptibility of Te atoms in the liquid alloys should be determined. However, there is no exact information on the ionization state of Te atom in the liquid state as far as the authors are aware. The susceptibility of the Te^{2+} ion was taken here, the value of which was taken from the paper of Nasu *et al.*,[17] based on the result that 2.5 electrons per atom enter the conduction band in liquid Te.[16] Figure 7 includes the result using the susceptibility of Te^{4+} ion together. The result for the susceptibility criterion when using the susceptibility of Te^{2+} ion, indicates a fair agreement with that from the conductivity data except for the Ag_2Te rich region. This magnetic susceptibility approach, however, gives only a rough estimate on electron localization because of the strong dependence on the accuracy of ion susceptibility data tabulated by various researchers.

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