

## Electrical behavior of liquid semiconductor alloys $\text{Tl}_X\text{Se}_{100-X}$

H. Rasolondramanitra and M. Cutler

*Physics Department, Oregon State University, Corvallis, Oregon 97331*

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The temperature dependence of the electrical conductivity  $\sigma$  and the thermopower  $S$  of liquid  $\text{Tl}_X\text{Se}_{100-X}$  has been measured as a function of composition in the range  $X \leq 55$ . An unusual effect of composition on  $S(T)$  is observed when  $X$  is decreased below 23 at. % Tl. This is interpreted in terms of a contribution to transport of charge by ionic motion in addition to electronic motion. The electronic transport occurs in an acceptor band created by diatomic  $\text{TlSe}^-$  molecular ions. With the help of the bond equilibrium theory, the experimental results together with published information about the spin density are used in an analysis which yields quantitative information about the ionic and electronic transport processes at  $X \leq 31$ . The electronic behavior is examined in terms of the theory for a narrow impurity band, and evidence is found for the occurrence of an Anderson transition.

### I. INTRODUCTION

The Tl-Se system is one of many binary alloys which are liquid semiconductors with a  $p$ - $n$  transition at a stoichiometric composition ( $\text{Tl}_2\text{Se}$ ). After the first observations of the liquid semiconductor properties,<sup>1</sup> systematic studies of the electronic transport behavior have been reported by several groups.<sup>2-4</sup> The interpretation of these experimental results has been reviewed by one of us,<sup>5</sup> particularly in comparison with the analogous and better understood system Tl-Te. There are many similarities between the two systems, but a striking difference is that the large thermopower  $S$  and small electrical conductivity  $\sigma$  in the Se-rich compositions indicate that the Fermi energy is well above the valence-band edge in the Se-rich alloy.

This difference offers a favorable opportunity to investigate the molecular and electronic changes which occur as increasing amounts of an electropositive element (Tl) are added to a chalcogen (Se). In the Tl-Te system, where a semimetallic situation prevails between the compositions Te and  $\text{Tl}_2\text{Te}$ , interpretation of the changes is made difficult by the poor understanding of the molecular and electronic structure of Te. This is much better understood in principle in the case of Se, although the difficulties due to uncontrolled impurities have so far prevented the interpretation of the transport properties of liquid Se. The study by Petit and Camp<sup>4</sup> of the electrical conductivity  $\sigma$  in the composition range  $X \leq 38$  for  $\text{Tl}_X\text{Se}_{100-X}$  represents an investigation along these lines.

The measurement of the thermopower  $S$  in conjunction with  $\sigma$  provides a more powerful means for investigating the electronic structure, since the value of  $S$  can often be related to the distance of the Fermi energy  $E_F$  from the energy  $E_c$  of the conducting states. Then one can derive from  $\sigma$  the conductivity of the conducting states  $\sigma(E_c)$ , and from that, information about the density of these states.<sup>5</sup> In prior work,  $S$  has not been studied at  $X < 40$ . In this paper we report measurements of  $\sigma$  and  $S$  in the composition range  $0 < X \leq 55$ . Our results for  $S$  show a very unusual behavior at  $X < 23$ , which indicates that ionic

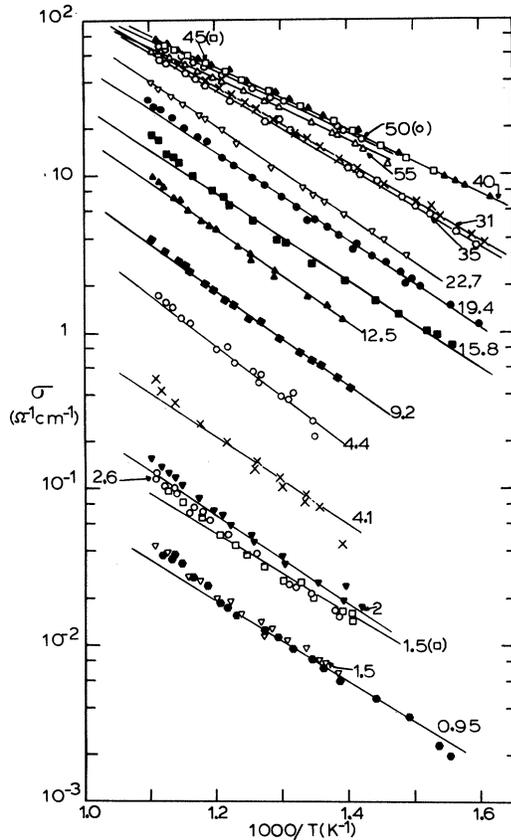
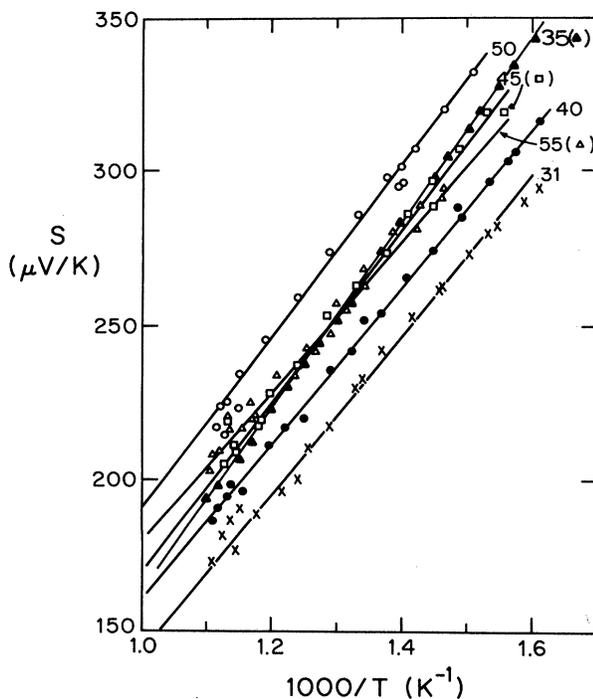
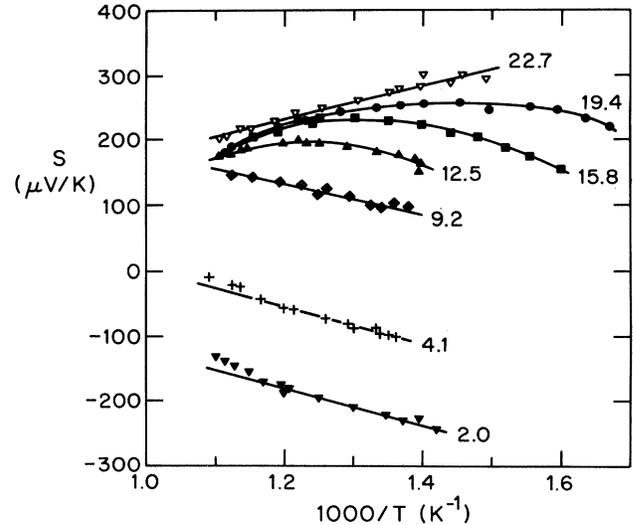
transport plays a significant role at small  $X$ . Ionic transport has been observed previously in conjunction with electronic transport in metal-molten-salt alloys such as BiI<sub>3</sub>-Bi (Ref. 6) and Cs-Au (Ref. 7). This is the first time it has been observed in a chalcogenide alloy.

It has been possible to analyze the behavior of  $\sigma$  and  $S$  in conjunction with magnetic susceptibility data<sup>8,9</sup> with the help of a theory for molecular equilibrium which takes into account the polymeric structure of the liquid.<sup>10,11</sup> The analysis yields detailed information about the two transport mechanisms, ionic and electronic. The latter is particularly interesting because it occurs in a narrow acceptor band, and we believe that observed behavior reflects the appearance of localization due to an Anderson transition. In the following section (Sec. II), the experimental results are presented, and the analysis of the behavior at  $X \leq 31$  is carried out in terms of established theoretical models in Sec. III. We examine the physical implications of the results in Sec. IV.

### II. EXPERIMENTAL RESULTS

Our results for  $\sigma$  are shown in plots of  $\ln \sigma$  versus  $T^{-1}$  at various compositions in Fig. 1. The activation energies do not change greatly with  $X$  and are generally in the range 0.4–0.6 eV. For  $X < 23$ , there is a small but distinct increase in slope at the high-temperature end of the range at a number of compositions. The shallow maximum in  $\sigma(X)$  in the range between  $X=30$  and  $X=60$ , and the rapid drop when  $X$  decreases below 30 is in accord with previous reports, and the quantitative agreement is fairly good.

The thermopower data are presented in plots of  $S$  versus  $T^{-1}$  in Figs. 2 and 3. At  $X > 31$ , the activation energies do not change much with  $X$ , and have values which are smaller than those for  $\sigma$  by 0.11–0.25 eV. As  $X$  decreases below 23, a striking change occurs. A negative shift, starting at low  $T$ , causes  $S(T)$  to go through a maximum. As  $X$  decreases, the negative shift increases in magnitude until there is a straight line with a negative

FIG. 1.  $\ln \sigma$  vs  $1/T$  at various compositions  $X$ .FIG. 2.  $S$  vs  $1/T$  at various compositions  $X \geq 31$ .FIG. 3.  $S$  vs  $1/T$  at various compositions  $X < 23$ .

slope at  $X=9.2$ . At this composition,  $S$  is still positive. A further decrease in  $X$  causes  $S$  to decrease further without much change in slope, until it is negative.

At low concentrations of Tl ( $X < 4$ ), we were not able to obtain consistent results with different samples. We believe that this was caused by oxygen impurities which we have been unable, so far, to eliminate. This problem is an extension of a similar problem observed by us and others in measurements on liquid selenium.

### III. INTERPRETATION OF THE ELECTRONIC BEHAVIOR

#### A. Molecular structure

The large increase in  $\sigma$  as Tl is added to Se is similar to that observed when the monovalent elements Tl, Ag, Cu, and Na are added to  $\text{Te}_{0.5}\text{Se}_{0.5}$ , and is explained by a similar molecular mechanism.<sup>12,13</sup> Selenium atoms are normally covalently bonded with twofold ( $2F$ ) coordination. In addition, there are small concentrations of bond-defect atoms: onefold- ( $1F^-$ ) bonded Se atoms which have a negative charge ( $D_S^-$ ) or are dangling-bond atoms, i.e., neutral but paramagnetic ( $D_S^*$ ), and threefold- ( $3F^-$ ) bonded positive ions ( $D_S^+$ ).<sup>10</sup> The resulting structure is a polymeric mixture of chains and rings. The added Tl is expected to form  $1F$  ( $M_1$ ) centers which reduce the average chain length and inhibit the formation of rings. As in the case of the doped  $\text{Te}_{0.5}\text{Se}_{0.5}$  alloys, the rapid increase in  $\sigma$  with  $X$  implies that added transport occurs in acceptor states associated with the Tl atoms. This leads to the hypothesis that the acceptor states are formed by diatomic molecules  $\text{TlSe}^-(D_M^-)$  and  $\text{TlSe}^*(D_M^*)$  which have a relatively high concentration as the result of an attractive interaction between  $1F$  bond-defect Se atoms and the  $1F$  Tl atoms. There are theoretical reasons for expecting this to occur, which are discussed in Ref. 12. This hypothesis is supported by a rapid increase in spin density when Se is doped by Tl, as observed in magnetic susceptibility measurements. Below we shall present a quantitative evalua-

tion of the concentrations of the  $D_M^*$  centers by comparison of the magnetic susceptibility data with theoretical expressions derived from the bond equilibrium theory.

The bond equilibrium theory (BET) provides relatively simple expressions for the concentrations of bond defects and molecular configurations associated with impurities.<sup>10,11</sup> They are identical with expressions derivable from the law of mass action for defect centers in crystals, except for a "polymer factor"  $p_n$ . The polymer factor reflects the effect on the statistical distribution of polymer chains when an  $n$ -F atom is part of a polymer chain. The expressions for the concentrations of the pertinent centers (denoted by a small  $d$  instead of the capital  $D$  for the center itself) are

$$d_S^* = p_1 X_S \exp(-\beta g_S^*), \quad (1)$$

$$d_S^- = p_1 X_S \exp(-\beta g_S^- + \beta E_F), \quad (2)$$

$$d_S^\dagger = p_3 X_S \exp(-\beta g_S^\dagger - \beta E_F), \quad (3)$$

$$d_M^* = X_M X_S \exp(-\beta g_M^*), \quad (4)$$

$$d_M^- = X_M X_S \exp(-\beta g_M^- + \beta E_F), \quad (5)$$

where  $\beta = 1/kT$ , and  $E_F$  is measured from the position of the top of the valence-band edge at  $T=0$ .  $g_i$  is the free energy of formation of an  $i$  center from atoms in their normally bonded state, and all concentrations are normalized to the concentration of atoms  $N_a$  ( $\approx 2.7 \times 10^{22}$  cm<sup>-3</sup>). The values of the fugacities  $X_S$  for Se and  $X_M$  for Tl are determined by the requirement that the concentrations of the Se and Tl in the various constituents add up to the values required by the overall composition. Most of the Tl atoms are normally bonded, chain-terminating atoms  $M_1$  whose concentration is given by

$$m_1 = p_1 X_M. \quad (6)$$

Since  $m_1 \approx x$  ( $= X/100$ ),  $X_M \approx x/p_1$ .

The values of the polymer factors  $p_1$  and  $p_3$  depend on the total concentrations  $c_n$  of  $n$ -fold constituents, as discussed in Ref. 10. In the present case,  $c_1$  ( $\approx x$ ) is much larger than  $c_3$  except when  $X \rightarrow 0$ , and  $p_1$  and  $p_3$  have limiting values which are independent of  $c_3$ . It is useful to make an evaluation of  $p_1$  and  $p_3$  which is somewhat different from that in Ref. 10. In the latter, the derivation is based on an approximation to the sum of concentrations of polymer molecules which is inaccurate when the average molecular size is small. Since small molecules have relatively high concentrations at large  $X$ , we have used a summation which is more accurate in that limit, and also assume that  $c_3 \approx 0$ . With these changes, the results for  $p_n$  and other pertinent parameters are

$$p_1 = [6(2-3x)]^{1/2}, \quad (7)$$

$$p_3 = \frac{2(1-x)^2}{[6(2-3x)]^{1/2}}, \quad (8)$$

$$X_M = \frac{x}{[6(2-3x)]^{1/2}}, \quad (9)$$

$$X_S = \frac{(2-3x)}{2(1-x)}. \quad (10)$$

## B. Concentration of the acceptor states

The  $D_M^*$  and  $D_M^-$  centers generate empty and filled sites in the acceptor band. It has been possible to determine their concentrations as a function of  $T$  and  $X$  in the range  $X \lesssim 31$  from experimental data for the spin density and the thermopower, with the help of the BET.

The paramagnetic susceptibility  $\chi_p$  is due to dangling bonds on Se atoms which are attached either to Se chains ( $D_S^*$ ) or Tl atoms ( $D_M^*$ ), so that the spin density  $d_s$ , derived by use of the Curie law, can be equated to  $d_M^* + d_S^*$ . From Eqs. (1), (7), and (10), we can write

$$d_S^*(x) = d_S^*(0) [1 - (3x/2)]^{3/2} / (1-x), \quad (11)$$

where  $d_S^*(0)$  is to be obtained from the spin density of pure Se. From the data of Gardner and Cutler,<sup>14</sup>  $d_S^*(0) = \exp(3.25 - 0.682/kT)$  so that Eq. (11) permits calculation of  $d_M^*(x)$  from  $d_s(x) - d_S^*(x)$ . This result is to be compared to

$$d_M^*(x) = \frac{x}{2\sqrt{6}} \frac{(2-3x)^{1/2}}{1-x} \exp \left[ -\frac{e_M^*}{kT} + \frac{s_M^*}{k} \right], \quad (12)$$

obtained from Eqs. (4), (9), and (10). In doing this, we have assumed that  $m_1 = x$ , and expressed  $g_M^* = e_M^* - Ts_M^*$  in terms of the enthalpy and entropy of formation of  $D_M^*$ . It was found that the experimental results of Misonou *et al.*<sup>9</sup> were in best accord with this theoretical result. By taking into account the predicted dependence of  $d_M^*$  on  $x$ , a best fit to their data for the two highest Tl concentrations ( $x=0.20$  and  $0.26$ ) was used to obtain the parameters  $e_M^* = 0.415$  eV and  $s_M^*/k = 3.86$ . The BET curves with these empirical values of the free-energy parameters agree with the experimental curves from Ref. 9 within a few percent. The behavior of  $d_M^*$  at compositions measured in the present study were calculated from Eq. (12), and the dependence on  $T$  is shown in Fig. 4.

The concentrations of the  $D_M^*$  and  $D_M^-$  centers are related to the distance of the Fermi energy from the center of the acceptor band  $E_A$  by

$$2d_M^-/d_M^* = \exp[(E_F - E_A)/kT]. \quad (13)$$

If the acceptor bandwidth is less than  $kT$ , electronic transport in the acceptor band occurs essentially at  $E_A$ , so that the thermopower is given by

$$S_E = (E_F - E_A)/eT. \quad (14)$$

Therefore, Eqs. (13) and (14) permit calculation of  $d_M^-$  from  $d_M^*$  in the narrow-band limit provided that  $S_E$  is known.

As noted in Sec. II, there is an unusual effect of composition on the behavior of  $S$  when  $X < 23$ . As will be discussed in Sec. III C, this is caused by a negative contribution due to ionic motion which decreases  $S$  below  $S_E$ . In order to evaluate the ionic contribution as well as to determine  $d_M^*$ , we need to determine  $S_E$  at compositions  $X < 23$ , where it cannot be measured directly. This can be done with the help of Eq. (14) if the BET equations are used to extrapolate the behavior of  $E_F - E_A$  at  $X \geq 23$  to smaller values of  $X$ . This can be justified if the ionic equilibrium process which determines the behavior of  $E_F$

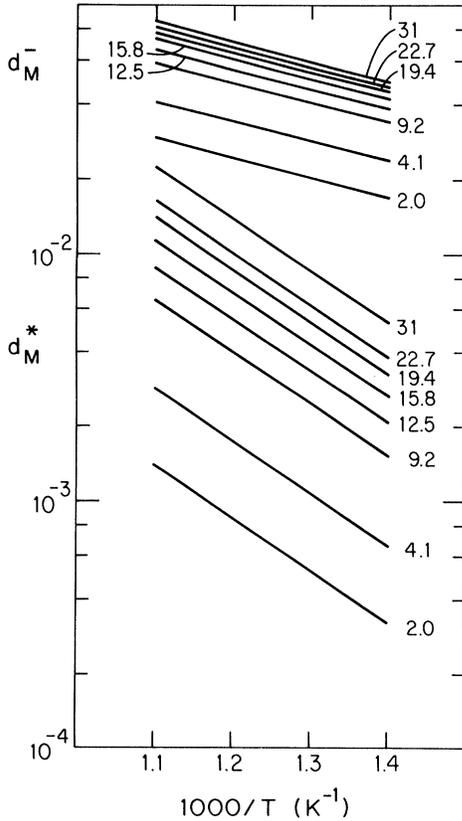


FIG. 4.  $\ln d_M^*$  and  $\ln d_M^-$  vs  $1/T$  at various compositions  $X$ . The upper curves correspond to  $d_M^-$ .

remains unchanged. We can assume that the dominant negative ion is  $D_M^-$  down to the smallest  $X$  in the experimental range, and that the dominant positive ion is  $D_S^+$  when  $X$  is small. At large  $X$ , one can expect at some point that  $Tl^+$  or positive ions derived from  $Tl^+$  by clustering to Se chain atoms, such as  $Tl_3Se^+$ ,  $-Se(Tl_2)^+$  or  $-(SeTl)^+$ , will become important. The dependence of  $E_F$  on composition is determined by equating the concentrations of the dominant positive- and negative-ion species. If they are  $D_M^-$  and  $D_S^+$ , then Eqs. (3) and (5) together with Eq. (6) (with  $m_1 = x$ ) give

$$E_F = (g_M^- - g_S^+) / 2 + (kT/2) \ln(p_1 p_3 / x). \quad (15)$$

Substitution of Eqs. (7), (8), and (15) into Eq. (14) yields

$$S_E(x) = F_S(T) + (k/2e) \ln[(1-x)^2/x], \quad (16)$$

where all the terms independent of composition are lumped in the term  $F_S(T)$ .

According to Eq. (12),  $S_E$  decreases with  $x$ . The increase in  $S$  with  $x$  for  $X < 23$  is ascribed to the effect of ionic transport. If one plots isotherms of  $S$  based on the data of Figs. 2 and 3, one finds only a small decrease at  $X = 31$ , followed by another gradual increase at  $X \geq 40$ . This suggests that the assumptions leading to Eq. (16) are breaking down at  $X \geq 30$ . We have therefore somewhat arbitrarily assumed that  $S \approx S_E$  at  $X = 23$  and 31, and have used the average value of  $F_S(T)$  obtained at these two compositions to extrapolate  $S_E$  into the range  $X > 23$ .

$F_S(T)$  in  $V/K$  was found to be

$$F_S = 0.254/T - 1.258 \times 10^{-4}. \quad (17)$$

The values of  $d_M^-$  are then obtained from Eqs. (13) and (14), and are plotted in Fig. 4.

### C. Effect of ionic transport on the thermopower

In electronic transport, an electron tunnels between a  $D_M^*$  center and a  $D_M^-$  center. The other transport mechanism is drift of a  $D_M^-$  ion. The thermodynamic theory of irreversible processes<sup>15</sup> provides phenomenological expressions for the thermopower which encompass both mechanisms:

$$S = \sum_i t_i (Q_i - \mu_i) / q_i T, \quad (18)$$

where  $t_i$  is the fraction of the current carried by particle  $i$  with a chemical potential  $\mu_i$ , heat of transport  $Q_i$ , and charge  $q_i$ . In the present problem  $\mu_i = E_F$  and  $q_i = -e$  for both mechanisms. When an electron tunnels from a  $D_M^-$  center to a  $D_M^*$  center, the enthalpy  $e_M^-$  is moved forward with the electron, and  $e_M^*$  moves in the opposite direction, so that  $Q_E = e_M^- - e_M^*$ . Thus the electronic term is

$$S_E = -(e_M^- - e_M^* - E_F) / eT. \quad (19)$$

Since the acceptor-state energy  $E_A = e_M^- - e_M^*$ , this is identical to the narrow-band result in Eq. (14). For the ionic mechanism,  $Q_I = e_M^-$ , so that

$$S_I = -(e_M^- - E_F) / eT. \quad (20)$$

Combining these terms in Eq. (18), the result can be written<sup>16</sup>

$$S = t_E S_E + t_I S_I = S_E - t_I e_M^* / eT. \quad (21)$$

Thus the negative shift in  $S$  at  $X < 23$  is to be accounted for by increasing values of  $t_I$ . Using the value  $e_M^* = 0.415$  eV obtained from the fit of  $d_s$  data to the BET, values of  $t_I$  were calculated from experimental data for  $S$  together with the extrapolated values of  $S_E$ .

If the ionic and electronic contributions to the transport occur independently, then  $\sigma$  is the sum of the contributions  $\sigma_I$  and  $\sigma_E$ , respectively, so that  $\sigma_I = t_I \sigma$  and  $\sigma_E = t_E \sigma$ . To show that this is so, we consider the expressions for  $\sigma_E$  and  $\sigma_I$  in terms of the diffusivity of  $D_M^-$  centers. The expression for  $\sigma_I$  is straightforward,

$$\sigma_I = (e^2/kT) D_I d_M^- N_a. \quad (22)$$

The formula for the electronic conductivity in a narrow band can be written in the form

$$\sigma_E = (e^2/kT) N_a D_E 2d_M^- d_M^* / (2d_M^- + d_M^*), \quad (23)$$

where  $D_E$  is the electronic diffusivity. From this, one can see that the tunneling process between  $D_M^-$  and  $D_M^*$  centers gives the  $D_M^-$  centers an effective electronic diffusivity

$$D_{\text{eff}} = D_E [2d_M^* / (2d_M^- + d_M^*)], \quad (24)$$

where  $D_{\text{eff}}$  bears the same relation to  $\sigma_E$  as  $D_I$  does to  $\sigma_I$ .

In terms of  $D_{\text{eff}}$ , the overall diffusivity of the  $D_M^-$  centers is  $D_{\text{eff}} + D_I$ . This is the justification for regarding the transport as the sum of two independent processes.

#### IV. DISCUSSION

In Fig. 5,  $\ln\sigma_E$  and  $\ln\sigma_I$  are plotted versus  $T^{-1}$  at compositions for which reasonable numerical accuracies can be expected for  $t_E$  and  $t_I$ , respectively. It is seen that the activation energies for  $\sigma_E$  are generally greater than for  $\sigma_I$ . The increasing ratio  $\sigma_E/\sigma_I$  with  $T$  explains the increases in slope of  $\ln\sigma$  with  $T$  in Fig. 1.

The activation energies of both  $\sigma_E$  and  $\sigma_I$  decrease with  $X$ . This implies a similar behavior for the activation energies of  $D_I$  and  $D_E$  since we have assumed constant activation energies for  $d_M^*$  and  $d_M^-$ . [In the case of  $\sigma_E$ ,  $d_M^* \ll d_M^-$ , so that Eq. (23) implies that  $\sigma_E \sim D_E d_M^*$ .] There is reason to believe, however, that this assumption is not correct for  $d_M^-$ . A variation of  $e_M^-$  with composition can be expected to affect the derived values of  $t_I$  and  $t_E$ , and thus  $\sigma_I$  and  $\sigma_E$  for  $X < 23$ , as well as the values of  $d_M^-$ . Therefore, before discussing the implications of the results for  $D_I$  and  $D_E$ , it is desirable to evaluate the magnitude and significance of the possible errors due to this assumption.

Because of the large polarizability of the Tl atoms, the change in dielectric screening with composition can be expected to affect the energies of formation of  $D_M^-$  and  $D_S^+$  ions. There is no experimental information about the value of the macroscopic dielectric constant  $K$ , and even if it is known, the effect of  $K$  on the value of  $e_M^-$  and  $e_S^+$

is difficult to determine theoretically. We have made a rough estimate for  $K$  based on a linear interpolation of values derived from  $K$  for solid TlSe and Se, which is  $K = 37.8x + 5.2$ . We shall use this to estimate the changes in  $e_M^-$  and  $e_S^+$  with composition by assuming that they vary as  $K^{-1}$ . This is expected to overestimate the influence of composition.

The value of  $d_M^-$  is determined from the BET equations (3) and (5) by using the condition of electrical neutrality ( $d_M^- = d_S^+$ ) to eliminate  $E_F$ . The result is that the ion density has an activation energy  $e_I = (e_S^+ + e_M^-)/2$ . The value  $e_I = 0.12$  eV, corresponding to the slope of the  $d_M^-$  plots in Fig. 4, can be expected to be accurate for  $X = 23$  and 31, but may be larger for smaller values of  $X$ . In extrapolating to obtain  $S_E$  at compositions  $X < 23$ , we have also assumed that the enthalpy terms in  $E_F - E_A$  do not depend on composition. Since  $E_A = e_M^- - e_M^*$  and  $E_F$  has a term  $(e_M^- - e_S^+)/2$ ,  $E_F - E_A$  contains a term  $e_M^* - e_I$ . Upon going from  $X = 23$  to 9,  $K$  decreases from 14 to 9, and  $K \approx 6$  for  $X = 2$ . Assuming that  $e_I \propto K^{-1}$  gives values of  $e_I = 0.19$  and 0.28 at compositions  $X = 9$  and 2, instead of a constant value 0.12. The corresponding values of  $e_M^* - e_I$  are 0.22 and 0.14 instead of the constant value 0.30. We shall see below that the interpretation of the electronic transport results depends on information at compositions  $X = 31$  to 9, and the conclusions are not likely to be strongly affected by the errors in  $d_M^-$ . For the ionic transport discussion, which depends most strongly on data for  $X = 2$ , the quantitative uncertainties are much greater.

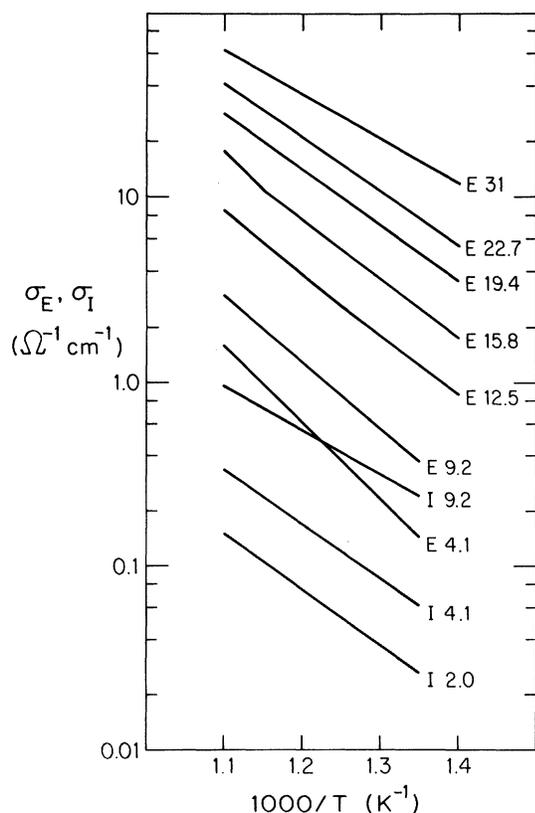


FIG. 5.  $\ln\sigma_E$  and  $\ln\sigma_I$  vs  $1/T$  at various compositions  $X$ .

#### A. Ionic transport

When  $D_I$  is calculated from Eq. (22), the results for  $X = 2$  are in good agreement with the Arrhenius relation  $D_I = 0.786 \exp(-0.50 \text{ eV}/kT) \text{ cm}^2/\text{sec}$ . At larger  $X$ ,  $D_I$  increases very roughly in proportion to  $X$ , and there are increasing deviations from a straight line with the same slope in an Arrhenius plot. This may reflect, in part, increasing numerical errors due to decreasing values of  $t_I$ .

The question we need to ask is whether the magnitude of  $D_I$  and the observed behavior, as a function of  $T$  and  $X$ , are in keeping with the expected behavior for a diatomic molecule dissolved in a liquid consisting of polymer chains with an average length  $2/x$ . The activation energy 0.50 eV is very close to the activation energy  $E_\eta$  of the viscosity  $\eta$  of Se in the same range of  $T$ .<sup>17</sup> This is in accord with a relationship between the diffusivity of a solute and the viscosity of the solvent, which is valid in many liquids,<sup>18</sup>

$$D_I = kT/ar\eta, \quad (25)$$

where  $a$  is a constant (equal to  $6\pi$  according to Stokes law) and  $r$  is the radius of the spherical volume corresponding to the volume of the  $D_M^-$  molecule. Since the viscosity of polymeric liquids increases with chain length, the observed increase in  $D_I$  with  $X$  is qualitatively in agreement with expectations.

We cannot use Eq. (25) directly to check the magnitude of  $D_I$ , because there are no measurements of  $\eta$  available in this range of  $T$  and  $X$ .<sup>19</sup> If it is assumed that  $D_I \propto x$ , a

rough check on the magnitude can be made by extrapolating either to  $x = \frac{2}{3}$  or  $x \approx 0$ . At  $x = \frac{2}{3}$ , the solvent molecules are small, comparable in size to water. The extrapolated ionic mobility  $eD_I/kT = 0.025 \text{ cm}^2/\text{V sec}$  is found to be comparable to typical values for simple ions in dilute aqueous solutions ( $\sim 0.06 \text{ cm}^2/\text{V sec}$ ). To make a comparison using  $\eta$  for Se, we extrapolate to a value of  $x$  such that the average molecular size  $2/x$  is equal to the value  $2/d_S^*(0)$  for Se. When this is done, assuming  $a = 6\pi$ , we find that Eq. (25) yields  $r = 3.8 \text{ \AA}$ . Thus, to the extent that it can be determined, the magnitude of  $D_I$  is consistent with the expectations for a  $D_M$  molecule.

### B. Electronic transport in the narrow acceptor band

The electronic behavior of narrow bands has been a subject of great interest in relation to the metal-nonmetal transition.<sup>20,21</sup> The classic examples are impurity bands in crystalline Si, and there has been considerable experimental and theoretical study of these and other narrow-band systems. Our results for the acceptor band in Tl-Se characterize a system which differs from most previously studied systems in several ways as the result of the liquid state. (1) The density of acceptor states  $N_A$ , and consequently the average separation distance  $R$ , changes with temperature as well as composition. (2) The thermal motion of the atoms causes temporal potential fluctuations on a time scale of  $\sim 10^{-12}$  sec, as well as spatial fluctuations. (3) The magnitude of the potential fluctuations can be expected to be  $\approx kT$ , rather than much greater than  $kT$  as in the case of solids at low  $T$ .

Since the average distance  $R$  between acceptor centers changes with  $T$ , it is best to examine the results in terms of electronic diffusion frequency  $\nu_d$  instead of  $D_E$ , where the two are related by

$$D_E = \nu_d R^2 / 6. \quad (26)$$

$R$  is calculated from the relation  $R = [6/\pi(d_M^- + d_M^*)N_A]^{1/3}$ . In Fig. 6 we have plotted  $\ln h\nu_d$  versus  $R$  for compositions  $X = 9.2$  to 31. Several features are to be

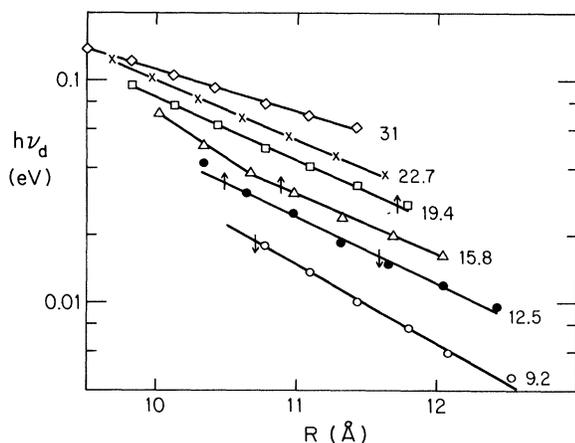


FIG. 6.  $\ln h\nu_d$  vs acceptor-center distance  $R$  at various compositions  $X$ . The distance where  $\sigma_A R = 1200 \Omega^{-1} \text{ cm}^{-1} \text{ \AA}$  is indicated by an arrow pointing up and the value  $600 \Omega^{-1} \text{ cm}^{-1} \text{ \AA}$  by an arrow pointing down.

noted. (1) The magnitude of  $h\nu_d$  ranges from  $\sim 0.15 \text{ eV}$  ( $\approx 2kT$ ) to less than  $0.006 \text{ eV}$ . At the low end,  $\nu_d$  is considerably less than the thermal vibration frequency. (2) The slopes of the curves are constant except for a discrete change in slope which occurs for  $X = 15.8$  and possibly also for  $X = 12.5$ . (3) The slopes tend to decrease with  $X$ .

The constant slopes in this plot suggest that  $\nu_d$  is closely related to the tunneling frequency  $\nu_E$  which is obtained from the transfer integral between two adjoining acceptor sites. From the tight-binding model described by Mott and Davis,<sup>22</sup>

$$h\nu_E = I_0 \exp(-\alpha R), \quad (27)$$

where  $I_0$  is a slowly changing function of  $R$  and  $\alpha$  is the decay rate of the wave function on an isolated site. But the magnitudes of  $h\nu_d$  at the two extremes of the range indicate that it reflects transport by extended electron states at the high end, and by localized states at the low end. This suggests that the sharp change in slope, which occurs at  $X = 15.8$  and possibly also at  $X = 12.5$ , corresponds to an Anderson transition.

Mott has discussed extensively the theory for localization in a narrow band.<sup>22</sup> The key parameters are the potential fluctuation  $V_0$  and the bandwidth  $B$  in the absence of fluctuations. Tight-binding theory gives  $B = 2z h\nu_E$  where  $z$  is the coordination number. Anderson localization occurs when  $V_0/B$  has a critical ratio whose value is uncertain, but most likely is  $\sim 2$ . The region where the slope changes at  $X = 12.5$  and  $15.8$  coincides very well with  $kT/h\nu_d = 2$ .  $kT$  seems to be a very likely value for  $V_0$  in a liquid. On the other hand, the relation of  $h\nu_d$  to  $B$  is very uncertain and complicated.

Another way of looking at the localization question is to compare the conductivity  $\sigma_A$  of the acceptor-band states with Mott's estimate of the minimum metallic conductivity  $\sigma_M$ . According to Mott,  $\sigma_M R = C$  where  $C = 610 \Omega^{-1} \text{ cm}^{-1} \text{ \AA}$  according to the most likely estimate. There is some evidence that  $C$  might be  $\sim 2$  times larger than that.<sup>23</sup>  $\sigma_A$  is related to  $\sigma_E$  by

$$\sigma_A = \sigma_E \exp(eS_E/k), \quad (28)$$

and we find that the regions where the slopes for  $X = 12.5$  and  $15.8$  change coincide with  $\sigma_A R = 1200 \Omega^{-1} \text{ cm}^{-1} \text{ \AA}$ . For neighboring compositions, the largest value of  $\sigma_A R$  is  $580 \Omega^{-1} \text{ cm}^{-1} \text{ \AA}$  for  $X = 9.2$ , and the smallest value is  $1165 \Omega^{-1} \text{ cm}^{-1} \text{ \AA}$  for  $X = 19.4$ . This therefore supports the conclusion that the change in slope is caused by an Anderson transition.

Why should the Anderson transition cause a change in slope of  $\ln \nu_d$  versus  $R$ ? A speculative answer is suggested by a rough understanding of the dependence of  $\nu_d$  on  $\nu_E$  on the two sides of the transition. On the localized side, transport occurs by phonon-assisted hopping. The theory for this<sup>24</sup> indicates that  $\nu_d \propto \exp(-2\alpha R)$ . On the nonlocalized side of the transition, according to the Kubo-Greenwood formula,  $\nu_d$  is proportional to the square of the momentum matrix element, and should therefore have a factor  $\exp(-2\alpha R)$ . However, as the Anderson transition is approached, the fraction of delocalized states in the band is rapidly decreasing to zero, which may cause  $\ln \nu_d$  to decrease more rapidly than  $2\alpha R$ . If this interpretation

is correct, then the slopes on the localized side represent the values of  $2\alpha$ , so that  $\alpha=0.35 \text{ \AA}^{-1}$  at  $X=9.2$ . On the nonlocalized side, one may expect the slope to be  $\approx -2\alpha$  well away from the Anderson transition, so that one obtains  $\alpha=0.215 \text{ \AA}^{-1}$  at  $X=31$ .  $\alpha$  is related to the depth  $W$  of an isolated acceptor state by  $\alpha=2\pi(2mW)^{1/2}/\hbar$ , and since  $X$  can be expected to vary roughly as  $K^{-1}$ , the decrease in slope with  $X$  can be expected. Using the formula for  $K$  given at the beginning of this section, the ratio  $\alpha(31)/\alpha(9.2)$  is expected to be 0.72, compared to the ratio 0.61 inferred from the slopes.

## V. CONCLUSIONS

In summary, we have presented a coherent explanation of the behavior of  $\sigma$  and  $S$  in terms of transport due to acceptor centers formed from TlSe molecules. At large  $X$ , where  $d_M^-$  is large, electronic tunneling occurs in a narrow acceptor band. At smaller  $X$ ,  $d_M^-$  is smaller, and the tunneling probability falls to a point where ionic transport plays a significant role. This gives rise to a large negative contribution to the thermopower which has not been observed previously in liquid chalcogenide alloys.

It should be noted that a shift from electronic to ionic transport is an inevitable consequence of a decrease in the concentration of electronic states in a liquid because of the exponential decrease in the tunneling probability with distance. The only question is the magnitude of the conductivity at which it takes place, and that depends on the mobility of the ions. In the present case, the fact that the ions are small molecules causes the ionic transport to be visible at a relatively large value of  $\sigma$  ( $\approx 1\Omega^{-1}\text{cm}^{-1}$ ). The numerical values determined for the electronic and ionic diffusivities are somewhat uncertain because of the effect of composition on parameters related to the energies of charged centers, which cannot be predicted theoretically with any precision. But the general magni-

tudes are reasonable for the various processes which play a role.

Our model for transport is in direct conflict with the conclusions of Petit and Camp,<sup>4</sup> who interpreted their results at  $X < 3$  in terms of electronic tunneling between thallium atoms. It seems difficult to justify an electronic tunneling model in this composition range unless a large fraction of the thallium atoms can participate in the tunneling process. Otherwise, the tunneling probability would be too small because  $R$  is too large. However, one needs, in addition, another state of the Tl atom with a different charge, which is the result of the transfer of charge in tunneling. The conductivity expression will contain the equilibrium concentration of this state [analogous to  $d_M^*$  in Eq. (23)], and if one takes this factor into account, the experimental electronic mobility seems to be too large to be physically reasonable.

No analysis of the experimental results for  $X > 31$  has been made in this paper. At first, we expected that the number of states in the acceptor band would continue to increase with increasing  $X$ . With this assumption, it is difficult to explain the observed behavior of  $S$  and  $\sigma$ , which do not change much with increasing  $X$ , or else reverse the direction of change. We now believe that  $d_M^*$  and  $d_M^-$  go through a maximum at  $X \approx 40$ . This conclusion is supported by the fact that the spin density also has a maximum at this composition.<sup>8</sup> An explanation of this behavior requires a refinement of the BET which takes into account differences in bond energies of the polymer molecules when their average length becomes small. We are currently working on this problem, and its solution will be the basis of efforts to extend the interpretation of the electronic behavior to these compositions.

## ACKNOWLEDGMENT

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