

Electronic Properties of Liquid Semiconductor Solutions of Thallium and Tellurium*

M. CUTLER†

General Atomic Division of General Dynamics Corporation, John Jay Hopkins Laboratory for Pure and Applied Science, San Diego, California

and

Physics Department, Oregon State University, Corvallis, Oregon

AND

C. E. MALLON

General Atomic Division of General Dynamics Corporation, John Jay Hopkins Laboratory for Pure and Applied Science, San Diego, California

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Experimental data for the resistivity and Seebeck coefficient of liquid thallium-tellurium solutions have been analyzed in the light of the conventional equations for electronic structure and transport in solids. The behavior of p -type solutions can be described by the presence of deep acceptor levels which have an activation energy of 0.25 ± 0.01 eV. The hole mobility μ_p in these solutions is nearly independent of composition with $d \ln \mu_p / d \ln T = -1.68 \pm 0.08$ over a large range of T . Data are obtained about the variation of the concentration of acceptor states with composition. Preliminary information is also obtained about the energy of the band gap, and the mobility of n -type solutions. The results show that much of the observed behavior can be placed in the framework of conventional theoretical equations. We discuss some of the ways in which these equations may require significant modifications in the case of liquid semiconductors, and note how this would change our numerical results.

I. INTRODUCTION

COMPARED with our knowledge of solids, our present understanding of the electronic structure of liquid semiconductors is in a rudimentary state. This status is indicated by the absence of an appreciable body of studies relating experimental information to theoretical equations. Ioffe and Regel¹ have written a review which covers most of the work which has been done in this field.¹ Much of it has been aimed at simply establishing experimentally the existence of semiconductor behavior in the liquid state, or explaining theoretically why this should be possible. The most extensive investigations have been made with liquid tellurium and solutions containing selenium.^{1,2} These have not been very successful in elucidating the electronic behavior, although the physical structure of these liquids seems to be fairly well understood.

The first observations of the semiconducting properties of liquid thallium-tellurium solutions were made by Stoneburner,³ who measured the Seebeck coefficient and the electrical conductivity as a function of temperature, at compositions corresponding to the solid compounds Tl_2Te_3 and $TlTe$. Data for the electrical conductivity of liquid Tl_2Te have been published

recently by Katilene and Regel.³ In an investigation of the thermoelectric behavior of the Tl - Te solutions by the present authors,⁴ these transport parameters were measured over a wide range of compositions, and a study was also made of the thermal conductivity.⁵ It was found that the thermoelectric figure of merit has large values at some ranges of temperature and composition.

Of more interest from a basic viewpoint, we have observed that a p - n transition occurs at a composition of approximately 66.5 at. % of thallium, with n -type liquids occurring on the thallium-rich side of this boundary. Much of the data in Ref. 4, and further data obtained subsequently, have been found susceptible to analysis in terms of the formulas of conventional theories for the semiconductor behavior of solids. The analysis, which is the subject of the present paper, leads to some insight into the electronic structure of the Tl - Te solutions. It also provides some background for determining the applicability of the conventional theory to liquid semiconductors.

There is considerable question about the applicability of conventional theories for band structure and electronic transport to semiconductors in the liquid state. The usual transport theory is based on the assumption that the mean free path of carriers is longer than the de Broglie wavelength. This is not likely to be true for liquid semiconductors.¹ It also seems possible that the density of states at the band edges will have a dependence on the energy which is significantly different from the quadratic equation usually applicable in solids. Although the derivations of conventional theories make use of assumptions which are not valid

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† Present address: Physics Department, Oregon State University, Corvallis, Oregon.

¹ A. F. Ioffe and A. R. Regel, *Progress in Semiconductors*, edited by A. F. Gibson (John Wiley & Sons, Inc., New York, 1960), Vol. 4, p. 239.

² M. Cutler and C. E. Mallon, *J. Chem. Phys.* **37**, 2677 (1962); A. Epstein, H. Fritzsche, and K. Lark Horowitz, *Phys. Rev.* **107**, 412 (1957).

³ D. F. Stoneburner, *Trans. AIME* **233**, (1) 153 (1965); E. R. Katilene and A. R. Regel, *Fiz. Tverd. Tela* **6**, 2869 (1964) [English transl.: *Soviet Phys.—Solid State* **6**, 2284 (1965)].

⁴ M. Cutler and C. E. Mallon, *J. Appl. Phys.* **36**, 201 (1965).

⁵ C. E. Mallon and M. Cutler, *Phil. Mag.* **11**, 667 (1965).

for liquids, the resulting equations are not necessarily incorrect. One of the goals of our research program is to learn to what extent the experimental behavior of liquid semiconductors is consistent with the predictions of conventional theory.

It will be seen that at least some aspects of conventional theories do apply to our data. However, caution must be applied in a detailed application of the theoretical formulas. It would not be surprising if some finer aspects of the theory are not correct while the grosser ones are correct. We therefore take a conservative approach in making interpretations of our results and try to make a distinction between the analytical results themselves and their possible implications or interpretations in terms of conventional theoretical concepts.

II. DATA AND ANALYSIS

A. Over-all Behavior

The curves shown in Figs. 1, 2, and 3 contain the data for the resistivity ρ and Seebeck coefficient S which are used in this paper. They show the dependence on the absolute temperature T and the composition X (atomic percent of thallium) and include some data reported previously, as well as new data. The experimental techniques used in making these measurements are discussed in Ref. 4.

Solutions with $X \geq 66.5$ are n type, and the rest are p type. ρ and S for the strongly n -type solutions ($X=67.5$ and 68) have a relatively weak dependence on T , suggesting that the electron concentration is nearly constant. The rapid decrease in ρ and S with increasing T for the solutions near $X=66$ is typical of intrinsic behavior. However, the strong temperature dependence persists for much lower values of X , even

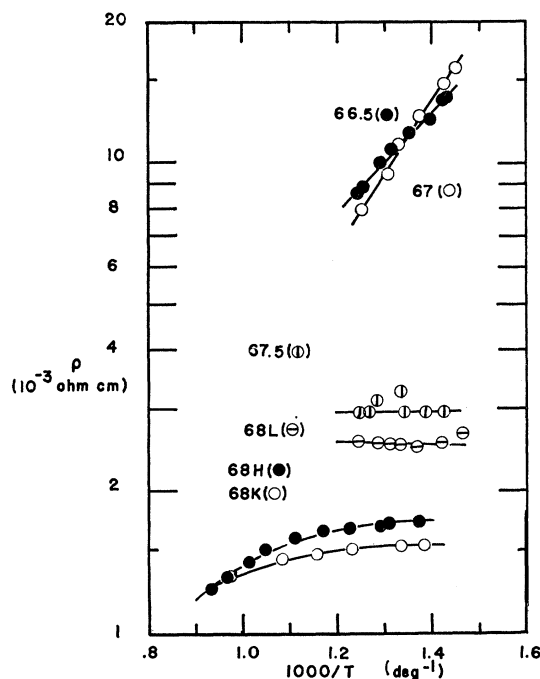


FIG. 1. Resistivity curves for n -type solutions.

though S and ρ become relatively small for a given T . This behavior, as well as the weak dependence of S and ρ on X as one goes in the p -type direction (as compared with the n -type direction), can be explained by the hypothesis that tellurium in excess of the intrinsic composition introduces deep-lying acceptor levels.

A clearer picture of the effect of composition is obtained from some isotherm curves for $\rho(X)$ and $S(X)$ reproduced in Fig. 4 from Ref. 4. The peak in ρ and

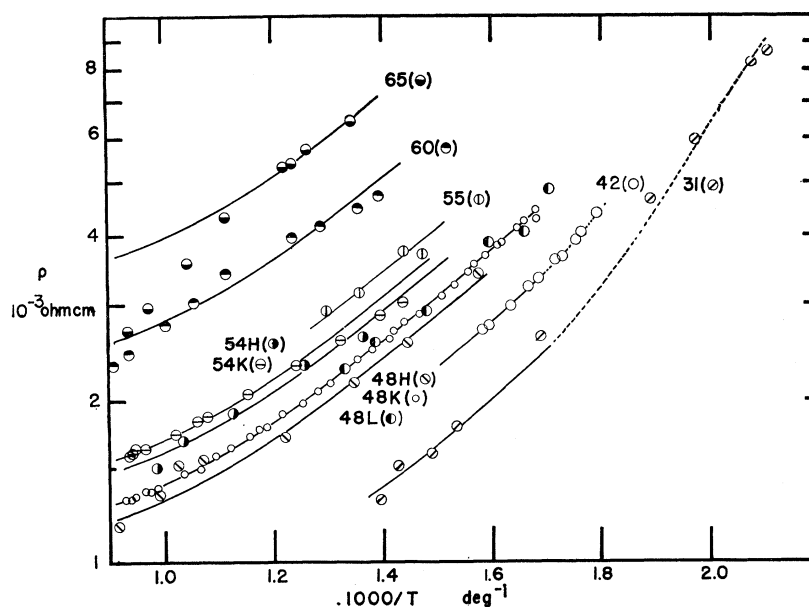


FIG. 2. Resistivity data for p -type solutions. Solid lines represent the fit of a common curve to data for the different compositions.

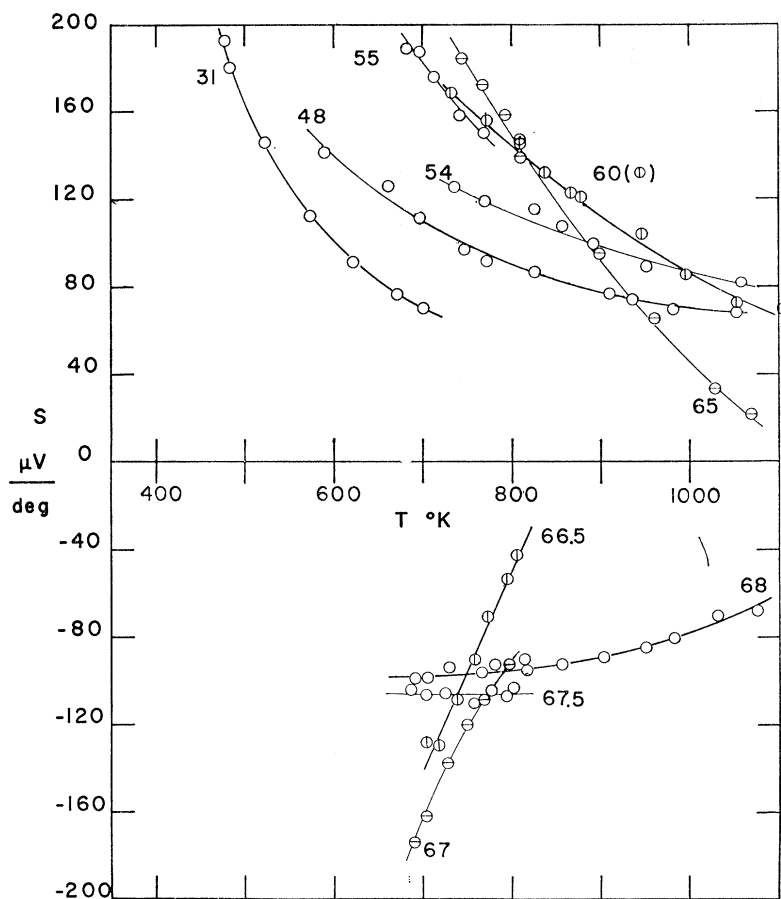


FIG. 3. Seebeck coefficient as a function of temperature and composition (at. % thallium).

the inversion of S from a maximum to a minimum value is what one would expect for a monotonic increase in the Fermi energy as X increases. It corresponds to nonstoichiometric doping with an intrinsic composition near $X=66.5$. The asymmetry can be explained if only a small fraction of the acceptor levels are ionized, whereas all of the donors (or a large fraction) are ionized.

Several different curves for $\rho(T)$ are shown for $X=68$. They were obtained with samples prepared at different times. This shows a strong sensitivity to the deviation from the stoichiometric composition, and limited experimental control of the composition. It is caused by the fact that the oxide scum on the liquid thallium was removed by allowing the molten pure metal to flow into the cell on filling it leaving behind a small but uncontrolled amount of metal. The molten tellurium does not seem to form a significant oxide scum. The sequence of solutions $X=67.5$, 67.0 , and 66.5 were prepared by adding small amounts of tellurium to a cell containing originally 68% thallium. As a result, the increments in this sequence of compositions are accurate, although the exact values are uncertain. This leads to an uncertainty (we estimate $\Delta X = \pm 0.5\%$) in the intrinsic composition, which is nominally between

66.0 and 66.5% thallium. Within this accuracy, the intrinsic composition corresponds to the formula Ti_2Te .

The behavior of the p -type solutions is much less sensitive to composition. A number of different measurements were made at some of the compositions. These different experiments are differentiated by a letter L , H , or K after the composition.

B. P-Type Solutions

The qualitative behavior of ρ and S for the p -type solutions suggests that the hole concentration p is governed by the concentration of acceptor states with deep-lying levels, as noted above. We can therefore write

$$p = p_1 \exp(-E_1/kT), \quad (1)$$

where p_1 depends on the composition (X), but is regarded as being independent of temperature, for the time being. The electrical conductivity σ of extrinsic p -type solutions is equal to $e\mu_p p$, where μ_p is the mobility, so that substitution of Eq. (1) for p gives

$$\sigma = e\mu_p p_1 \exp(-E_1/kT). \quad (2)$$

μ_p is a function of T , and might also depend on X .

According to Eq. (2), if μ_p depends only on T , or if its dependence on X can be expressed as a factor which is independent of T , experimental plots of the resistivity $\rho(T)$ with logarithmic scale for the dependent variable should yield parallel curves for different compositions X . This is what is found, as seen in Fig. 2. The solid lines in Fig. 2 represent a common curve (based on the more precise data of X_{48K}) shifted vertically to overlap the data at appropriate points. The data for $X=65$ and $X=60$ show evidence of conduction by minority carriers, as expected by the proximity to the intrinsic composition. Consequently, the common curve was matched to the data at the low-temperature end of the range. The data for $X=42$ and $X=31$ extend beyond the range of the reference curve, and the extension is indicated by dashed lines.

These results indicate that the temperature dependence of μ_p is invariant with composition to a high degree. It is possible, however, that there is some dependence on X in μ_p , which occurs in a factor which is independent of temperature. That is, we may conclude that $\mu_p = a(X)f(T)$, where $a(X)$ may or may not have an appreciable dependence on X . We shall see later that there is some indication of a relatively small dependence on X . However, for the time being, we ascribe the entire shift in ρ to changes in $p_1(X)$. From the measured shifts in the common curve in Fig. 2, we calculated the ratio of p_1 to the value for sample $54H$. These are plotted in Fig. 5 as a function of X . We will discuss this result later.

The ordinate in Fig. 2 is T^{-1} , so that the slope indicates approximately the value of E_1 . This is not extremely large compared to kT , so that the variation of μ_p with T causes a pronounced curvature. The determination of the value of E can be made without the complication of the temperature dependence of μ_p by means of an analysis of data for S which is analogous to the one for ρ .

The hole concentration is low enough so that Maxwell-Boltzmann statistics are applicable in most of the experimental range of X and T , but not all of it. Although the more accurate Fermi-Dirac statistics are used in our analysis, it is helpful to discuss the analysis first in the context of the Maxwell-Boltzmann approximation, where the procedure is simpler to understand.

With Maxwell-Boltzmann statistics, the Seebeck coefficient for holes can be expressed

$$(e/k)S = A_p + \ln(N_v/p), \quad (3)$$

where N_v is the usual "effective" density of states of the valence band, given in conventional band theory by $2(2\pi m_p^* kT)^{3/2}/h^3$. A_p is a constant whose value is determined by the scattering mechanism. If we substitute Eq. (1) for p , and write N_v as $BT^{3/2}$, then Eq. (3) can be rearranged in the form

$$(e/k)S - \frac{3}{2} \ln T = (A_p + \ln B - \ln p_1) + E_1/kT. \quad (4)$$

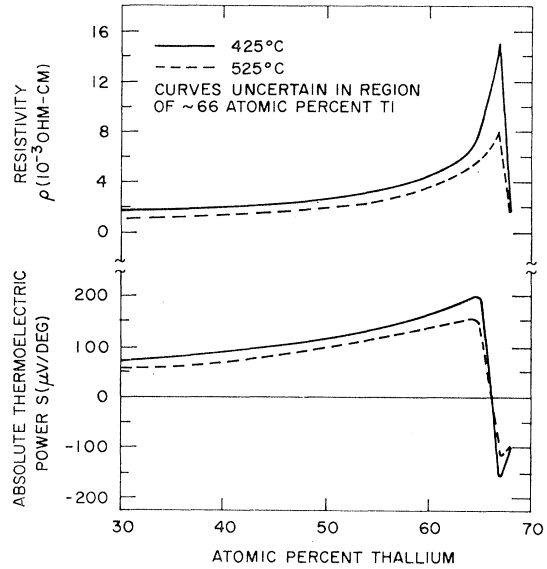


FIG. 4. Interpolated isotherms for ρ and S at $T=698$ and 798°K .

This suggests that the quantity on the left, which can be determined from experimental data, plotted as a function of T^{-1} , should yield a straight line with a slope equal to E_1/k . The results for different compositions should be the same straight line, displaced vertically through the dependence of p_1 on X . We found this to be the case, and subsequently used the value of E_1 , together with experimental data for $\rho(T)$ to determine the temperature dependence of the mobility, in the light of Eq. (2).

A more accurate procedure makes use of an equation for the Seebeck coefficient which is appropriate for Fermi-Dirac statistics:

$$Se/k = [(r+2)F_{r+1}(\xi)/(r+1)F_r(\xi)] - \xi. \quad (5)$$

ξ is equal to $(E_v - E_f)/kT$, and is related to p by

$$N_v/p = (2/\sqrt{\pi})F_{1/2}(\xi). \quad (6)$$

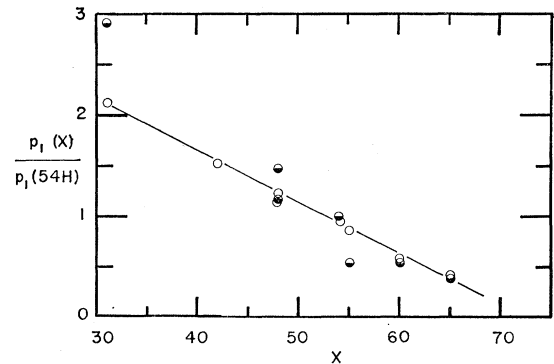


FIG. 5. Relative values of p_1 as determined from resistivity curves (open circles) and Seebeck coefficient data (partially filled circles). The ordinate is the ratio of p_1 at composition X to p_1 obtained from sample X_{54H} .

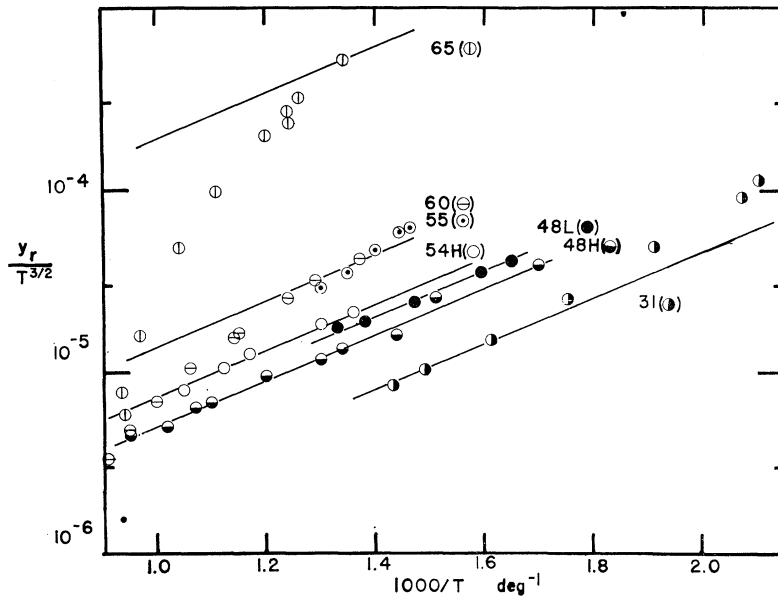


FIG. 6. Comparison of experimental data for $S(T)$ with the theoretical form of Eq. (8).

The functions $F_\nu(\xi)$ are the well-known Fermi-Dirac integrals, and the parameter r is determined from the dependence of the scattering time τ on the kinetic energy of holes ϵ through the equation $r = d \ln \tau / d \ln \epsilon$. In the Maxwell-Boltzmann limit where $-\xi \gg 1$, Eqs. (5) and (6) reduce to Eq. (3) with $A_p = \frac{5}{2} + r$.

One can write

$$N_v/p = y_r (Se/k), \quad (7)$$

where y_r expresses formally the dependence of N_v/p on S given by Eqs. (5) and (6). Then we obtain a more accurate relationship analogous to Eq. (4):

$$\ln y_r (Se/k) - \frac{3}{2} \ln T = (\ln B - \ln p_1) + E_1/kT. \quad (8)$$

The procedure is essentially the same as the one described for the Maxwell-Boltzmann expression, but one must assume a value of r to begin with. We chose $r = -\frac{1}{2}$, which was inferred by the earlier more approximate determination of the dependence of μ_p on T . We shall show later that this particular choice of r is not critical for our results.

The function in the left side of Eq. (8) plotted versus T^{-1} , calculated from experimental data for $S(T)$, is shown in Fig. 6 for various values of X . It is seen that a large part of the data falls on straight lines with a common slope which corresponds to $E_1 = 0.25 \pm 0.01$ eV. The negative deviations which occur in near-intrinsic compositions at large T can be identified with the effects of minority carriers. In addition to the high T deviations, there is a systematic increase in S above the theoretically fitted line which occurs at low T for $X = 31$. An explanation for this is proposed below.

Again, the vertical shifts required to superpose the curves in Fig. 6 determine the relative values of p_1 . These values of p_1 (normalized to the value for $X54H$)

are plotted in Fig. 5, as a function of X , together with the points derived from the resistivity curves.

The value of $p_{1S}(X)$ derived from the Seebeck coefficient (partially filled circles) show appreciably more scatter than those from the resistivity $p_{1R}(X)$ (open circles). The latter fall on a straight line which extrapolates to zero at $X = 72.5$. Because of the scatter, it is hard to tell whether there is a systematic trend with X in the ratio p_{1R}/p_{1S} . There is some indication of a trend for this ratio to decrease with increasing X . To the extent that there is such a trend, one can conclude that the mobility contains a factor $a(X)$ which varies with X . Our results indicate that $a(X)$ varies by less than a factor of 1.5 over the experimental p -type range of composition.

The availability of an accurate value for E_1 allows one to use Eq. (2) with experimental data for ρ to find $\mu_p(T)$ to an arbitrary constant. Because of the exponential, this procedure is sensitive to small errors in T . Rather than use all of the curves in Fig. 2 (superposed in accordance with the shifts in p_1) which leads to a rather fuzzy line for $\mu_p(T)$ in which $d \ln \mu_p / d \ln T$ is uncertain to about 30%, we used mainly data for a single composition ($X48K$). This was a measurement in which particular attention was paid to accuracy in T because of the need to use $d \ln \rho / dT$ for the determination of the thermal conductivity.

The results are shown in Fig. 7, where the quantity $\mu_1 (= \rho \exp(E_1/kT))$ represents the mobility to an arbitrary factor. The points fall on a straight line with a slope $d \ln \mu_1 / d \ln T$ equal to -1.68 ± 0.08 . This differs somewhat from the value -1.5 which is expected for thermal scattering in a solid. (The value -1.5 corresponds to $r = -0.5$.)

The resistivity data for samples $X42$ and $X31$ extend

to appreciably lower temperatures than the data for X48K. In order to get an indication of the trend of the mobility in this range, points were plotted in Fig. 7 which are based on the data for X42 and X31. The relative values of p_1 given in Fig. 5 were used to place them on the same mobility scale. Although these points show considerable scatter, they indicate a trend to a more positive value of $d \ln \mu_1 / d \ln T$. This suggests that another scattering mechanism with a larger value of r is becoming significant. One possibility is ionic scattering, where $r = +1.5$. In solid semiconductors, one frequently observes a maximum in $\mu(T)$ corresponding to a transition between ionic and thermal scattering.

The change in $d \ln \mu_p / d \ln T$ occurs in the same range of X and T as the one in which we have observed a positive deviation in S from the common curve (Fig. 6). This deviation is qualitatively consistent with the proposed change in the scattering mechanism. The added scattering by another mechanism with a larger value of r would cause an increase in the effective value of A_p . [It is proper in this range of T to use the Maxwell-Boltzmann approximation of Eq. (3); $A_p = 2.5 + r$.]

In the Maxwell-Boltzmann range, it is evident from Eq. (4) that varying values of A_p (or r) and m_p^* (which appears in B) would have an equivalent effect of merely shifting the vertical position of curves such as those plotted in Fig. 6. This remains very nearly true in the degenerate region in the range of values of r and ξ which was used in analyzing our data with the Fermi-Dirac functions of Eq. (8). As a consequence, our somewhat arbitrary choice of $r = -0.5$ (which corresponds in theory to $d \ln \mu_p / d \ln T = -1.5$ for thermal scattering) has no significant effect on our conclusions: an error in this regard is equivalent to having a somewhat different value of the unknown m_p^* .

C. N-Type and Intrinsic Solutions

The present data for $\sigma(T)$ and $S(T)$ of n -type and intrinsic solutions are not as amenable to quantitative interpretation as were the data for the p -type compositions. Some qualitative features have already been noted.

The n -type solutions X68K and X68H have nearly horizontal curves for $\rho(T)$ and $S(T)$, which start dropping in value more rapidly at the high temperature end. This is consistent with a system containing extrinsic electrons, and with thermally generated holes starting to appear at high T .

Some rough quantitative conclusions can be derived from a careful examination of the resistivity curves for X68K and X68H. If the donor ion concentration is N , then the conductivity can be written

$$\sigma = e\mu_n(N + p) + e\mu_p p. \quad (9)$$

In the range of T where $p \ll N$, we have, approximately,

$$p = n_i^2 / N = (N_c N_v / N) \exp(-E_G / kT), \quad (10)$$

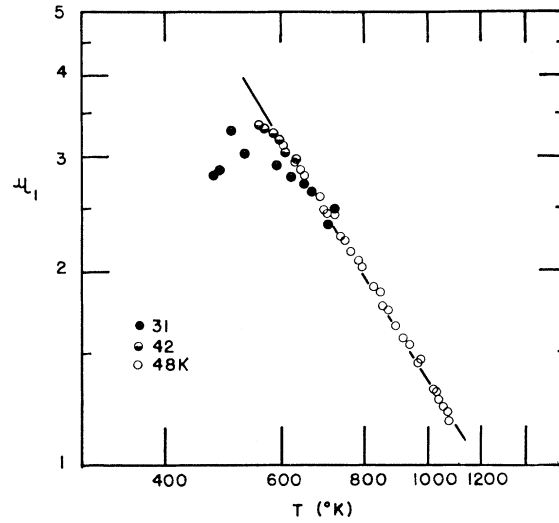


FIG. 7. The temperature dependence of the drift mobility of holes in arbitrary units, as defined in the text.

where N_c is the effective density of states in the conduction band. Since N is apparently larger for X68K than X68H, one would expect σ to decrease more rapidly with increasing T for the latter solution. In a range of T where $\sigma(X68H)/\sigma(X68K)$ is constant, presumably the extra conductivity due to holes is negligible for both solutions. This is observed to be the case between 450 and 525°K. In this range, σ for either solution increases by less than 2%, whereas T has increased by 18%. Therefore, $d \ln \mu_n / d \ln T$ is close to zero, in contrast to the results obtained for most of the p -type solutions. (We are assuming that μ_n is independent of composition in these n -type solutions.)

If one writes instead of Eq. (10)

$$p = (A/N) \exp(-E_2/kT), \quad (11)$$

where A is constant so that any T dependence of $N_c N_v$ is arbitrarily brought into the exponential, substitution in Eq. (9) gives

$$\sigma = (e\mu_n N) + e(\mu_n + \mu_p)(A/N) \exp(-E_2/kT). \quad (12)$$

The term $e\mu_n N = \sigma_N$ is the extrinsic conductivity, and the second term is the increase in conductivity due to the presence of minority carriers. If one assumes an appropriate value for σ_N , a plot of $\ln(\sigma - \sigma_N)$ versus T^{-1} should give a straight line, whose slope yields E_2 . This is found to be the case, but there is some latitude in the choice of σ_N , with corresponding changes in E_2 . Table I shows the results of such an analysis of the data for X68K and X68H. There is fair agreement between E_2 values for the two solutions. Another test of consistency is the ratio of $\sigma - \sigma_N$ at a given T , for the two solutions, which should be inversely proportional to N and hence the same as the inverse ratio of σ_N . This is reasonably close to being true, as seen in Table I. Other choices of σ_N would give somewhat different results,

TABLE I. Results of analysis of conductivity of *n*-type solutions.

Sample	X68H	X68K
σ_N	576 ($\Omega \text{ cm}$) ⁻¹	645 ($\Omega \text{ cm}$) ⁻¹
E_2	0.648 eV	0.679 eV
σ_N ratio (K/H)		1.12
$(\sigma - \sigma_N)$ ratio (H/K)		1.24

and perhaps worse consistency. On the basis of several attempts at curve fitting, we estimate that E_2 is equal to 0.65 ± 0.10 eV.

The electrical conductivities of X68L and X67.5 were in a temperature range which was too low to show minority carrier effects. X67 and X66.5, which both have negative values of S , have activation energies for the conductivity change with temperature of 0.256 and 0.178 eV, respectively (see Fig. 1). If they represented the temperature dependence of intrinsic carriers, one would expect the activation energies to be one-half the value of E_2 obtained from Table I, that is, about 0.32 eV. The decrease may reflect a transition in the equations of equilibrium to a situation where excitation of holes from acceptor states is playing an important role.

A further indication of the value of E_2 was obtained by the difference, due to minority electrons, between the experimental resistivity of X65 in Fig. 2, and the solid curve which represents the resistivity to be expected if only holes were present. A plot of $\Delta\sigma$ versus $1/T$ yielded a slope corresponding to $E_2 = 0.65 \pm 0.05$ eV in agreement with the results from *n*-type solutions.

The decrease on S with increasing T , and the rapid increase in the thermal conductivity of X68K (Ref. 5), are qualitatively consistent with the presence of holes as minority carriers. The curves $S(T)$ for X68H, X68K, and X68L were all very close to each other in contrast to the resistivity data. This reflects the fact that S depends on $\log n$, whereas σ is proportional to n . We did not find it possible to make any useful analysis of the S data.

III. DISCUSSION

We have noted previously two key questions about the applicability of conventional equations to electronic transport in liquid semiconductors: the effect of a relatively small scattering distance, and the nature of the distribution of states near the band edge. The former question has been discussed in some detail by Ioffe and Regel.¹ There are some indications in other systems that the results of the solutions of the Boltzmann transport equation have a validity that goes beyond the key assumption which goes into it, that the de Broglie wavelength is shorter than the scattering distance.⁶ In the case of metals, expressions have been derived for ρ and S which do not treat the electrons as particles between scattering events,⁷ but there is apparently no

such theory for semiconductors. The best procedure is to apply the conventional theory, but not to assume that it is valid in all detail. This seems to be justified by our present results.

The distribution of energy states at the band edge in a liquid semiconductor seems to be an open question at the present time. Edwards has presented some results for the band structure for a three-dimensional amorphous system,⁸ but some of the conclusions of this paper are disputed.⁹ At present, well accepted theoretical results are limited to one-dimensional systems.⁹ Another pertinent body of theoretical information comes from studies of band edges of solids which have high doping levels. In this case, there seems to be a Gaussian "tail" in the distribution of states near the original band edge,¹⁰ and a broadening and merging of shallow impurity states with the conduction (or valence) band. In addition to the spectral distribution of states at the band edge, there is a question about the relative contributions of the electrons in these states to electronic transport. For instance, electrons in the lowest energy states in the "tail" which arise from potential fluctuations may conceivably have relatively small mobilities.

Therefore it seems desirable to avoid complete commitment to the usual quadratic function for the density of states at the band edge. This quadratic distribution leads to the factor $T^{3/2}$ in N_v and in N_c , and is also intimately concerned in the definition of an effective mass.

Any expression of the form

$$\rho = (\text{const})T^b \exp(-E/kT) \quad (13)$$

will yield a nearly straight line in a plot of $\ln \rho$ versus T^{-1} , in a moderate range of T , provided that E is appreciable larger than $b\langle kT \rangle$. But instead of a slope $(-E/k)$, one would obtain a slope of $-(E + b\langle kT \rangle)/k$. Therefore, the activation energies obtained in the preceding section can be corrected in the light of any theoretical interpretation which requires a factor T^b in front of the exponential. However, we have in effect already assumed a particular factor in obtaining the activation energy of the acceptor states E_1 . This is a factor $T^{3/2}$ which was assumed in N_v in Eqs. (3)–(8). An effect occurs in the analysis of the Seebeck coefficient in these equations which is essentially similar to the one discussed above [Eq. (13)]. If the appropriate expression for N_v could be approximated in by an expression containing a factor T^b , then the results of our analysis would be modified to yield $E_1 - (3/2)\langle kT \rangle + b\langle kT \rangle$. In our experiments, the value of $\langle kT \rangle$ was about 0.077 eV. Of course, there is no reason to assume that N_v should properly be expressed as a power of T ;

⁸ S. F. Edwards, Proc. Roy. Soc. (London) **A267**, 518 (1962).

⁶ M. Cutler, J. F. Leavy, and R. L. Fitzpatrick, Phys. Rev. **133**, A1143 (1964); M. Cutler and J. F. Leavy, *ibid.*, **133**, 1153.

⁷ J. M. Ziman, Phil. Mag. **6**, 1013 (1961).

⁹ K. Hiroike, Phys. Rev. **138**, A422 (1965). This paper contains a review of the current status of such theories, and references to them.

¹⁰ E. O. Kane, Phys. Rev. **131**, 78 (1963).

we use this device mainly to illustrate some of the present ambiguity in the interpretation of our results.

In addition to this question, one would expect in normal theories that p_1 in Eq. (1) would contain a factor T raised to some power, depending on the dominant mechanism determining equilibrium between the acceptor states and the valence band. If the density of holes is equal to the density of acceptor ions N_{A^-} , then

$$p = (N_A N_v)^{1/2} \exp(-E_A/2kT). \quad (14)$$

N_A is the density of un-ionized states, which must be assumed, on the basis of the experimental results, to be much larger than p and N_{A^-} over most of the experimental range. In this case, a quadratic band edge leads to a factor $T^{3/4}$ in p_1 , so that the distance of the acceptor states from the band edge is 0.39 eV.

Another possibility is that $N_{A^-} \gg p$, in which case

$$p = (N_v N_A / N_{A^-}) \exp(-E_A/kT). \quad (15)$$

Then a quadratic band edge means that $E_A = 0.14$ eV.

Other more complicated models are conceivable. At the present time, there is little to guide one on the appropriate model. The first one is the simplest. For this model the data in Fig. 5 require that N_A increase with increasing amounts of tellurium. This is consistent with the usual result for binary semiconductors where a nonstoichiometric excess of the more electronegative element generally acts as a p -type impurity.

The same kind of reasoning applies to the interpretation of the activation energy E_2 for holes in n -type solutions. If we assume that there are quadratic band edges, $N_v N_c \propto T^3$. If, in addition, μ_n and μ_p are independent of T , as indicated by the behavior of σ , then we would conclude that $E_G = E_2 - 3(kT)$, or 0.42 ± 0.05 eV. It is interesting to note that this corresponds to an energy for the conduction band edge which is close to that of the acceptor states in the p -type solutions [for the model corresponding to Eq. (14)].

Since a $T^{3/2}$ factor was assumed in N_v in calculating E_1 , and this in turn was used in obtaining the T dependence of μ_p for the p -type solutions, any discrepancy would show up here also. If $N_v \propto T^b$, then $d \ln \mu_p / d \ln T = 1.68 + 1.5 - b$.

If we accept the numbers derived with the assumption that $N_v \propto T^{3/2}$, we observe that $d \ln \mu_p / d \ln T \simeq 0$ at $X = 31$ (and $T \simeq 200$ – 300°C), and decreases to -1.68 over most of the range of X and T . But $d \ln \mu_n / d \ln T \simeq 0$ for $X = 68$. One frequently has similar scattering mechanisms for holes and electrons in the same medium, so that these results suggest that there is a systematic trend in the scattering behavior. Possibly, the central range of X involves a behavior resembling thermal scattering in solids, and the behavior at the extremes

of the experimental range suggests that some ionic scattering may occur. In this connection, a change in the T dependence of μ may account partially for the smaller activation energies, noted above, for the resistivity curves of X67 and X66.5.

IV. CONCLUSIONS

Our analysis of the experimental data shows that a large part of the electronic transport data for liquid Tl-Te solutions can be placed into the framework of equations derived from conventional theories. The results for the p -type solutions were obtained with sufficient redundancy to make one confident that the numerical results are meaningful, although the extent to which certain factors in the equations can be safely used (like m^* , and $BT^{3/2}$ for N_v) is still open to question. The results obtained for the n -type solutions are much more marginal.

It is apparent that further studies, which provide more cross-references between the results of different measurements, are needed in order to explore further the extent to which conventional theoretical concepts can be applied, and possibly to learn where new ones must be developed. Along these lines, the concurrent use of measurements of the Hall effect should be very useful. This is included in a program of further study of liquid semiconductors currently at Oregon State University.

The main conclusions which have been derived include the following: Thallium-tellurium solutions behave like a binary semiconductor subject to nonstoichiometric doping with deviations from an intrinsic composition close to Tl_2Te . This composition region is also one in which the thermodynamic properties of the solutions show evidence of compound formation.¹¹ The tellurium-rich solutions have deep acceptor levels, with a well defined activation energy [0.25 eV, as defined in Eq. (1), subject to reservations discussed above]. The thallium-rich solutions give rise to extrinsic carriers, although minority carrier effects are observed at higher temperatures. The mobility of the tellurium-rich solutions is nearly independent of composition over a wide range of composition. Subject to the assumption that the electronic transport behavior is the same as what is expected when the band edge has a conventional distribution of states, we find that the mobility is proportional to $T^{-1.68}$ over most of the range of composition.

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¹¹ J. Terpilowski and E. Zaleska, *Roczniki Chem.* **37**, 193 (1963).