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Electric Properties of n-Type Liquid Alloys of Thallium and Tellurium*

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Measurements have been made of the electrical conductivity σ and Seebeck coefficient S of Tl-Te liquid alloys as a function of the composition X (at.% Tl) and temperature T for $67<X<72$. Also, the effects of doping the n-type binary solution with relatively small amounts of a third element were studied, with Ag, Cd, In, Sn, or Sb as the third element. In most ranges of T and X, there was little dependence of σ and S on T. It was possible to fit isothermal data to conventional transport theory in a rather comprehensive way. Plots of all data for σ versus S, including solutions containing a third element, fell on a single theoretical curve based on Fermi-Dirac integrals, corresponding to $r=-\frac{1}{2}$, viz., $\tau=\tau_1\epsilon^r$, where τ is the scattering time and ϵ is the kinetic energy of the electrons. This value of r, together with the finding that τ_1 is independent of T, indicates that scattering is caused by the intrinsic (nonthermal) disorder of the liquid. Comparison of the experimental dependence of S on the composition of Tl-Te solutions, with the theoretical dependence of the electron concentration n on S, shows that n is proportional to the concentration of Tl in excess of the composition Tl_2Te. Use of the same theoretical curve for the dependence of S on the concentration A of the various doping elements showed again a linear dependence. Comparison of the relative slopes dn/dA for the different elements indicates that one could assign integral valences as follows: Tl, +3; Ag, +1; Cd, +2; In, +1; Sn, +2; Sb, −1. Consideration of other aspects of transport theory, particularly the relative magnitudes of the de Broglie wavelength and the scattering distance, suggests that a large fraction of the electron charge in the conduction band is localized as the result of screening of the potential of the donor and acceptor ions. Solutions of the nonlinear Thomas-Fermi screening equation indicate that physically reasonable magnitudes of the effective dielectric constant K leads to value of α, the fraction of free-electron charge, which are consistent with the range of values required by the transport parameters. We deduce that $0.15\lesssim\alpha\lesssim0.5$, and the effective-mass ratio m^*/m lies between 1.0 and 2.0, corresponding to $K<10$.

I. INTRODUCTION

THE thallium-tellurium liquid alloy system has an electronic behavior which falls in the semiconductor or semimetallic category over a wide range of composition X (at. % Tl) and temperature T. Previous studies of this system,[1,2] based on measurements of the electrical conductivity σ and Seebeck coefficient S, have established two very interesting facts: (a) There is a p-n transition with changing composition which occurs at a composition very close to Tl_2Te. (No solid phase is known with this composition.) (b) The data for S and σ in the p-type range of compositions can be analyzed in the light of conventional concepts and equations for semiconductor transport behavior, and have been shown to fit these equations in a rather detailed way.[2] In particular, it was found that the p-type liquids have deep acceptor levels with a well-defined activation energy (0.25 eV), whose concentration varies with X. Also, the mobility varies roughly as $T^{-3/2}$ between 600 and 1200°K, which indicates phonon scattering.

The apparent agreement with conventional theory, found so far in Tl-Te, is very interesting because the assumptions upon which this theory is based have a dubious validity in liquids which are not metallic.[2,3] The point of view of our work is to examine the experimental behavior in detail in order to determine the extent to which conventional concepts of semiconductor behavior and the corresponding theoretical equations can be applied to liquids, and to determine where modifications must be made. The Tl-Te system is a good subject for such a study, and the present paper presents some further results of this investigation.

We are concerned here with a further study of S and σ in the n-type region of the Tl-Te system (the at. % of Tl, $X>66.7$), and an investigation of the effects of adding small amounts of various elements as a third constituent. We find, again, that it is possible to fit the data to conventional theory, in an even more detailed way than was possible for the p-type compositions.

The effect of adding excess Tl or Te to a liquid at composition originally at intrinsic composition Tl_2Te ($X=66.67$) can be regarded as ordinary nonstoichiometric doping. (Further justification of this statement will be given in Sec. IV.) Excess Te creates deep acceptor states which are only partially ionized.[4] Excess Tl creates donor states which are apparently fully ionized. As a result, the carrier concentration, as reflected in σ and S, changes slowly with X, and rapidly with temperature T, for the Te-rich, p-type compositions ($X<66.7$). It changes rapidly with X and slowly

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[1] M. Cutler and C. E. Mallon, J. Appl. Phys. 36, 201 (1965).

[2] M. Cutler and C. E. Mallon, Phys. Rev. 144, 642 (1966).

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

[4] Note that our results cannot distinguish between situations in which holes are created with or without a significant rearrangement of atoms in the liquid. Although the designation "acceptor states" in solids usually applies to the latter situation, both are quite possible in liquids. For brevity, we will also refer to the former case as involving acceptor states, even though the ionization process may include an extensive rearrangement of atoms, so that the un-ionized states do not exist in the usual sense.

with T for the Tl-rich, n-type compositions ($X>66.7$). This over-all behavior is illustrated in Fig. 1, which shows some isotherms for $\rho(X)$ (resistivity) and $S(X)$. Because of the great sensitivity of electron concentration n to X, earlier data[1,2] for $X>66.67$ were inaccurate because X was not determined with sufficient accuracy. The present work has included the development of techniques for determining the composition more accurately than was done in the past, and therefore provides data which are more suitable for analysis.

Some earlier preliminary studies have included an investigation of doping with some third element at strongly p-type compositions ($X\simeq31$).[5] It was found that very little change occurred in the electrical properties on addition of Bi, In, I, and Se. This negative result was understood later when the existence of deep, largely un-ionized acceptor states was recognized.[4] The un-ionized states would tend to keep the hole concentration nearly constant, since the addition or removal of holes by some other agency would cause a shift in the equilibrium between the holes and these acceptor states in such a way as to oppose the change. This is an exact analog to the acidity buffering action in an aqueous solution containing a mixture of a weak acid and its salt. The deep-acceptor states form an electronic buffer system for holes. This effect would not be expected in the n-type region and, indeed, it is found that relatively small amounts of various third elements cause pronounced changes in σ and S. Both p-type and n-type doping behavior has been found among the elements which were studied. In order to avoid the complications arising from the interaction of the electrons added or removed by the doping elements with the valence band or acceptor states, as would occur in near-intrinsic compositions, the doping experiments reported here were done in extrinsic n-type compositions of Tl-Te.

The present data provide detailed information about the change in σ and S with the addition of known amounts of Tl to Tl_2Te, and with addition of known amounts of various doping elements to compositions of Tl-Te containing some Tl in excess of Tl_2Te. As noted above, σ and S change very little with temperature T. (There is a partial exception in the case of two of the doping elements which were studied; this will be discussed at the appropriate point.) The relationship between σ and S, which arises from their common dependence on the electron concentration n, was found to agree with the prediction of conventional theory for the case where the dominant cause of scattering is the intrinsic (frozen) disorder of the liquid. In addition, the change in σ or S with the concentration of excess thallium or a third element is consistent with a linear dependence of n on these concentrations. The proportionality constants, in turn, are commensurate with simple integer valences for the impurity ions, and these valences make sense chemically.

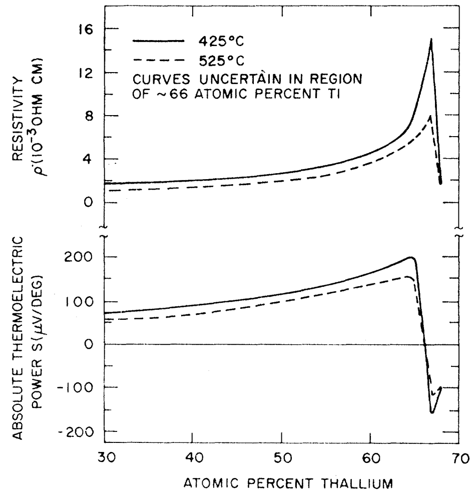

FIG. 1. Isotherms for the Seebeck coefficient and resistivity at $T=698$ and 798°K (from Ref. 1).

One might expect, at first sight, that n would be equal to the density of electrons released by the impurity ions. However, there are reasons to believe that only a fraction of these electrons move freely in the conduction band, and many of them are trapped in the potential wells of the parent ions in a manner discussed by Friedel[6] for the case of metallic alloys. The corresponding problem for semimetals is complicated by the poor applicability of presently available theory of screening. In Sec. IV, we discuss our results in terms of what is presently known about screening, and show

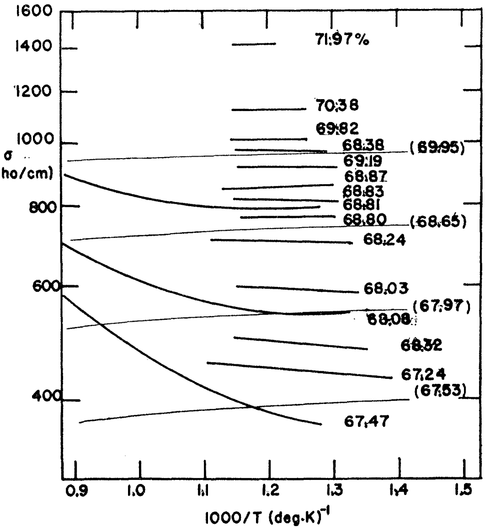

FIG. 2. Experimental and theoretical curves $\sigma(T)$ for various compositions X. The theoretical curves have thin lines, and their compositions are in parentheses.

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[5] M. Cutler and J. F. Leavy, Report No. GA4420, 1963, General Atomic, Division of General Dynamics, Inc., San Diego, Calif. (unpublished).

[6] J. Friedel, Advan. Phys. 3, 446 (1954).

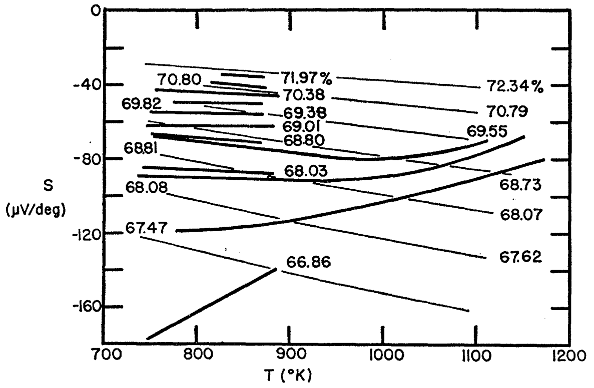

FIG. 3. Experimental and theoretical curves $S(T)$ at various compositions X. The theoretical curves are dashed, and their compositions are at the extreme right side of the figure.

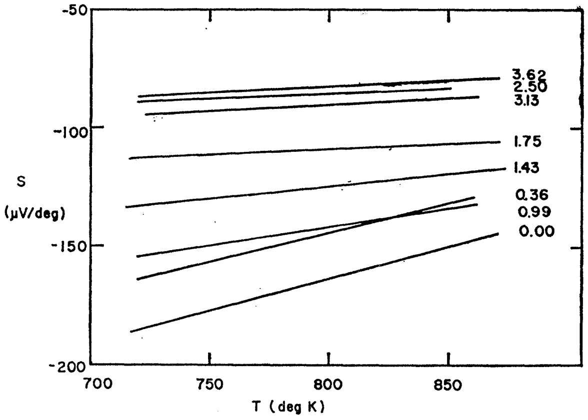

FIG. 5. Experimental curves $S(T)$ for various concentrations (A) of indium.

that they are consistent with a reasonable interpretation of the screening effects.

II. EXPERIMENTAL RESULTS FOR CONDUCTIVITY AND SEEBECK COEFFICIENT AS A FUNCTION OF COMPOSITION

A. Binary Solutions

The experimental method is largely the same as the one described in a previous paper.[1] Thallium has a strong tendency to oxidize in air, which causes a troublesome oxide film to occur on the liquid surfaces unless it is removed before placing the metal in the cell. In the past, we have found it effective to prepare solutions by causing the Tl to flow into the cell (which contains an inert atmosphere) from a glass container. The oxide remains behind on the container. But a small amount of Tl also remains behind, which leads to an uncertainty in the composition unless that amount is accounted for exactly. In the work reported here, the earlier technique was improved by making the container small enough to be weighed before and after addition of Tl, and by using a holder which could project the container in and out of the hot cell while the remainder of the sample remains molten. A flowing inert gas buffer arrangement near the mouth of the cell prevented air from going into the hot cell, and prevented vapors from escaping into the atmosphere during the time that changes were made in the composition. An important added advantage was that a number of changes of composition could be made and studied without the risk of cell breakage, which often occurs when the contents freeze.

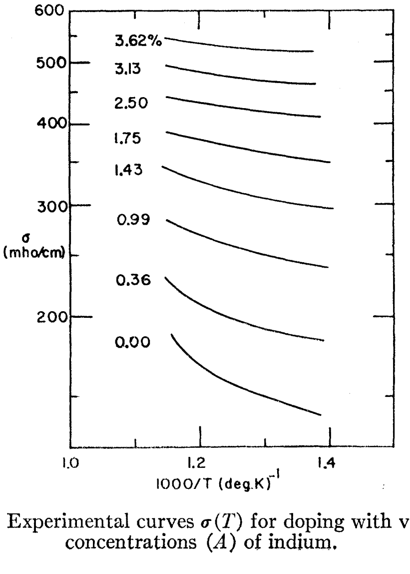

FIG. 4. Experimental curves $\sigma(T)$ for doping with various concentrations (A) of indium.

Using a glass cell for the most part, we obtained a number of curves for $\sigma(T)$ and $S(T)$ at various compositions X shown in Figs. 2 and 3. Curves ranging to temperatures above 850°K were obtained in fused quartz cells with sealed tungsten electrodes. Corrosion of the tungsten, to form ultimately a high-resistance layer on the electrodes, limited the use of these cells, and most data were obtained in glass cells. Except at temperatures above our normal range (>600°C) and at compositions approaching 67%, there is little change in σ and S with temperature. Most of the experimental information is contained, then, in isothermal curves for $\sigma(X)$ and $S(X)$. Our analysis is based on isothermal data, taken at $T=800$°K.

B. Doping Experiments

The effects of adding relatively small amounts of a third element to an initially n-type Tl-Te liquid were studied for cases where the third element was Ag, Cd, In, Sn, and Sb. The experiments are summarized in Table I. Except for Sb, they all showed n-type doping behavior, as indicated by increases in σ and decreases in the magnitude of S. Sb had the opposite effect, and thus is p-type. Ag, Cd, and In yielded curves for $\sigma(T)$ and $S(T)$ which are similar in shape to the Tl-Te curves. The results for In, shown in Figs. 4 and 5, are typical. The concentration is expressed in terms of A, the at. %

of the doping element. A ranged between 0 and 3.6 at. % in the various experiments. Sn and Sb had noticeably different temperature dependences. Figures 6 and 7 show $\sigma(T)$ for Sn and Sb. The $S(T)$ curves are not presented because the greater scatter in these data leads to a confusing pattern in the curves. But they reflect a similar effect, with $|S|$ increasing when σ decreases. We will discuss the implications of this temperature dependence in Sec. IV B. For the most part the over-all effect of doping can be described in the same way as it was for adding Tl to Tl_2Te: i.e., in terms of $\sigma(A)$ and $S(A)$ as measured at 800°K.

III. ANALYSIS OF ISOTHERMAL DATA AT 800°K

As noted in the Introduction, it has been possible to fit the experimental data to equations derived from conventional transport theory. For the present situation, the Fermi energy is near and generally above the conduction-band edge, so that one must use equations expressed in terms of Fermi-Dirac integrals.

Conventional theory provides solutions of the Boltzmann transport equation for σ and S, with the assumption that there is a simple isotropic relaxation process with a time constant τ.[7] τ depends on some power r of the kinetic energy ϵ, depending on the dominant scattering mechanism

$$\tau = \tau_0 \epsilon^r. \tag{1}$$

The density of states $g(\epsilon)$ at the band edge (ϵ_c) is derived from an assumed simple minimum of ϵ in wave-vector $(\mathbf{k})$ space. This leads to $g \propto (\epsilon - \epsilon_c)^{1/2}$, with a proportionality constant which reflects the curvature of $\epsilon(\mathbf{k})$, or the effective mass m^*. This, in turn, leads to a relation between the electron concentration n and the Fermi energy ϵ_f, expressed in terms of the reduced Fermi energy $\xi\ [=(\epsilon_f - \epsilon_c)/kT]$:

$$n = N_c \mathfrak{F}_{1/2}(\xi), \tag{2}$$

where

$$N_c = 2(2\pi m^* kT)^{3/2}/h^3, \tag{3}$$

and

$$\mathfrak{F}_\nu(\xi) = \frac{1}{\Gamma(\nu+1)} \int_0^\infty \frac{x^\nu dx}{e^{x-\xi}+1}. \tag{4}$$

We find it convenient to use the Fermi-Dirac integral $\mathfrak{F}_\nu(\xi)$ defined by Blakemore,[8] which differs from the

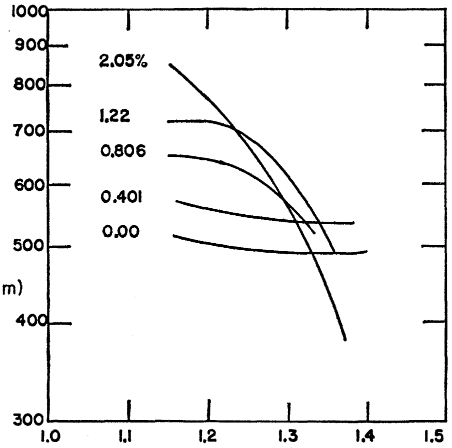

FIG. 6. Experimental curves $\sigma(T)$ for various concentrations (A) of tin.

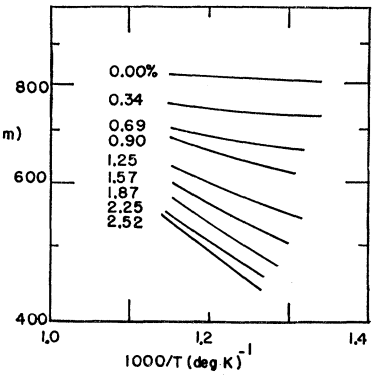

FIG. 7. Experimental curves $\sigma(T)$ for various concentrations (A) of antimony.

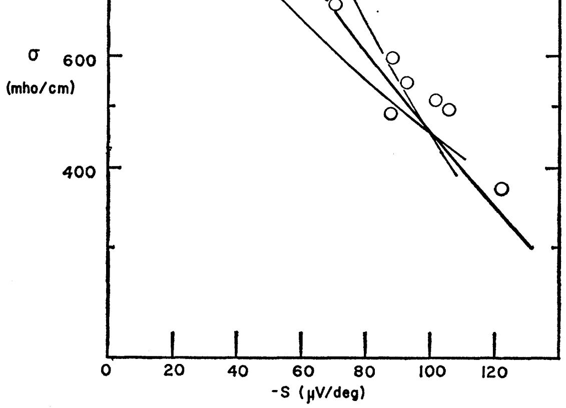

FIG. 8. Experimental points for σ versus S at 800°K for various binary solutions of Tl-Te. The heavy line is the theoretical curve for $r = -\frac{1}{2}$, and the light lines are for $r = 0$ and $r = 1$.

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[7] A. C. Beer, *Galvanomagnetic Effects in Semiconductors* (Academic Press Inc., New York, 1963); A. F. Ioffe, *Physics of Semiconductors* (Infosearch, London, 1960).

[8] J. S. Blakemore, *Semiconductor Statistics* (Pergamon Press, Inc., New York, 1962).

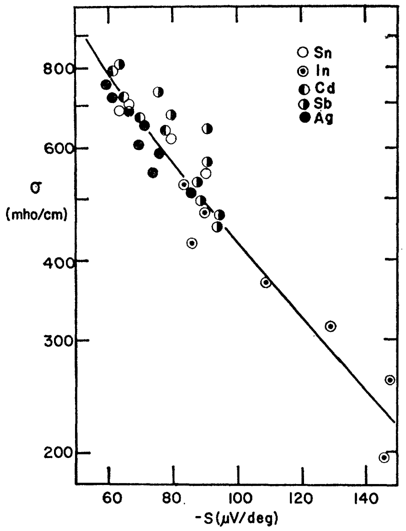

FIG. 9. Experimental points σ versus S at 800°K for solutions containing various small amounts of a third element. The solid line is the same theoretical curve ($r=-\frac{1}{2}$) as in Fig. 8.

usual one in being divided by the gamma function $\Gamma(\nu+1)$.

With the above assumptions, the transport theory yields

$$\sigma=\sigma_0\mathfrak{F}_{r+1/2}(\xi),$$

where

$$\sigma_0=(2e^2/3m^*)[\tau_0(kT)^r]N_c(r+\tfrac{3}{2}), \tag{5}$$

and

$$S=-(k/e)\{[(r+\tfrac{5}{2})\mathfrak{F}_{r+3/2}(\xi)/\mathfrak{F}_{r+1/2}(\xi)]-\xi\}. \tag{6}$$

The value of ξ is determined by the values of n and T, according to Eq. (2) and then σ and S depend on ξ and T through Eqs. (5) and (6), respectively, with r as a parameter.

Since T is fixed in considering isothermal data, σ will be a function of S, the relation being determined by the common dependence of σ and S on ξ for the appropriate r. In Fig. 8, we plot all available data points for Tl-Te (each one representing a different composition X at $T=800$°K) for σ versus S, putting σ on a log scale. From Eqs. (5) and (6), it is seen that the theoretical curve can be obtained by plotting $\mathfrak{F}_{r+1/2}(\xi)$ versus S, and the magnitude of σ_0 is determined by a vertical shift in the theoretical curve which matches it to the experimental curve. This was done for several values of r, and we found that the theoretical curve could be fitted uniquely with $r=-\frac{1}{2}$ as shown in Fig. 8. The light lines are for $r=-1$ and $r=0$. One sees that the slopes for these two values of r mismatch the experimental one to a significant degree, as compared to $r=-\frac{1}{2}$.

If adding a third element to Tl-Te does not change the scattering processes appreciably, but merely changes the electron concentration, then it should be possible to treat the experimental data for σ and S in the doping experiments in the same way, and fit them to the same curve. This is shown to be the case in Fig. 9. The theoretical curve is drawn with the same value of σ_0, equal to 182 mho/cm, as used in Fig. 8. The best fit for Fig. 8 alone yielded $\sigma_0=197$ mho/cm, and for Fig. 9 alone, 169 mho/cm.

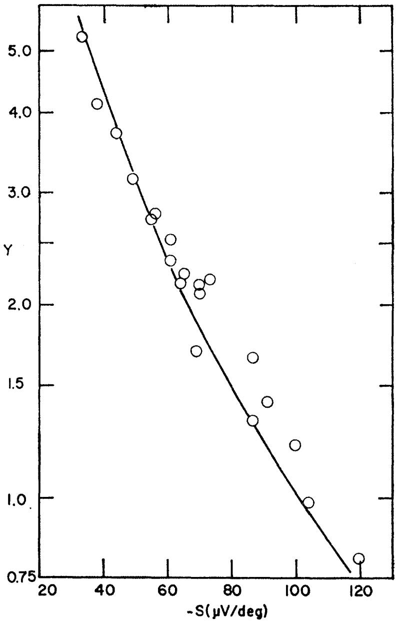

FIG. 10. Experimental points and theoretical curve ($r=-\frac{1}{2}$) for Y (at. % of Tl in excess of Tl_2Te) versus S.

Another result of the above analysis is that the value of ξ, and hence $\epsilon_f-\epsilon_c$, is determined for each composition. Given the deduced value $r=-\frac{1}{2}$, ξ can be inferred from the experimental value of S by Eq. (6). As shown in Fig. 13, $\epsilon_f-\epsilon_c$ increases from 0 to about 0.5 eV over the experimental range. Since $kT=0.069$ eV, the alloys should be classified as semimetallic over most of the range of composition.

The Tl atoms in excess of 66.67 at. % generate fully ionized donor centers. One would expect, then, that the total electron concentration n_t would be given by

$$n_t=3zN_a(Y/100), \tag{7}$$

where N_a is the number of atoms per cubic centimeter, Y is the at. % of Tl in excess of $Tl_2Te(Y=X-66.67)$, and z is the valence, i.e., the number of electrons released by each excess Tl atom by formation of charged donor centers.

On the other hand, the electron concentration n is related to the Seebeck coefficient S by Eq. (6). Knowing r, we can plot n versus S, and allow for the unknown factor N_c by a shift on the logarithmic scale for n. This is found to be nearly parallel to an experimental curve for Y versus S (with Y on a log scale), as shown in Fig. 10. This indicates that n is proportional to n_t so that the ratio α ($=n/n_t$) is constant over the experimental range of X.

TABLE I. Doping experiments.

Doping element	Maximum concentration (at. %)	Composition of original binary solution (at. % Tl)	dn_1/dA	Assigned valence z	$(1/z)(dn_1/dA)$	Deviation from ave $(1/z)(dn_1/dA)$
Ag	3.58	68.32	1.51	1	1.51	+8%
Cd	2.16	68.03	2.89	2	1.45	+3%
In	3.62	66.86	1.26	1	1.26	−10%
Sn	2.05	67.65	2.78	2	1.39	−0.7%
Sb	2.52	68.83	−1.32	−1	1.32	−6%
(Tl)			4.08	3	1.36	−3%
			Average of absolute values:		1.42	5%

It is worth pointing out that the various theoretical curves for S versus $\log n$, with different values of r, can be nearly superposed by a shift of the n scale. Therefore, the results here are not affected by the choice or r, except in the derived value of N_c.

The theoretical curve for n/N_c as a function of S can be used to deduce n/N_c as a function of the concentration A of the doping element, using experimental data for $S(A)$ at $T=800$°K. Although there is a large amount of scatter, n/N_c can be treated as a linear function of A. This is shown in Figs. 11 and 12, where n/N_c, denoted n_1, is plotted versus A for the different doping elements. The slopes of the experimental lines, dn_1/dA, can be compared with each other, and with the corresponding quantity dn_1/dX, already deduced for Tl. If the impurity atoms have a simple valence z and the fraction of free electrons α does not change, the slopes of the various lines should be commensurate with a set of integers. This is found to be the case, as shown in Table I. The slopes, divided by the assigned valences, agree with each other quite well, with a small standard deviation. The assigned valences are consistent with typical chemical valences of these metals. The observed valence of Ag (IB), Cd (IIB), and Tl (IIIB) correspond to complete ionization. The valences 1 and 2 for In (IIIB) and Sn (IVB) correspond to the retention of two s electrons, as is commonly observed for these elements in formation of compounds. The difference in behavior of Tl and In may possibly be caused by the smaller size of In ions. The valence −1 for Sb (VB) corresponds to acceptor formation with Sb^- imitating Te (VIB).

Multiplying the assigned numbers by an integer gives unreasonable numbers, and dividing by any factor leads to fractions. Although fractional valences are not impossible, because of the possibility of formation of complexes, the general consistency of the integral set with the typical chemical behavior argues strongly for the integral values. Hence we conclude

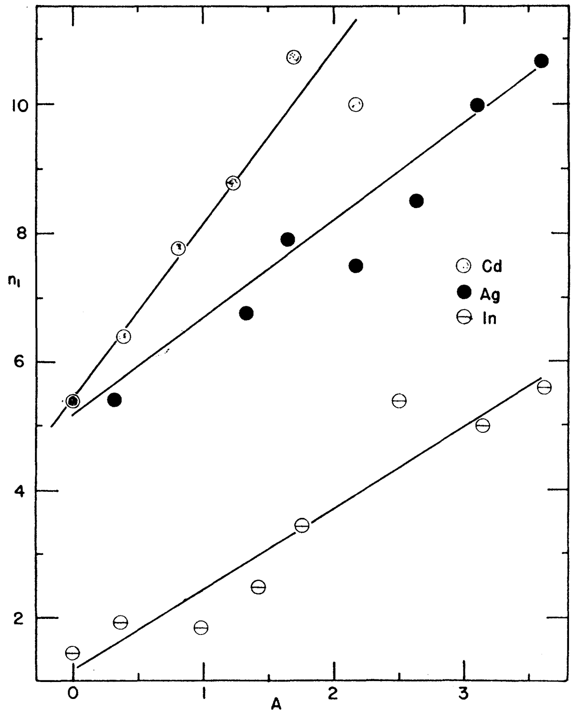

FIG. 11. Electron concentration, on arbitrary scale, versus concentration A for Ag, Cd, and In.

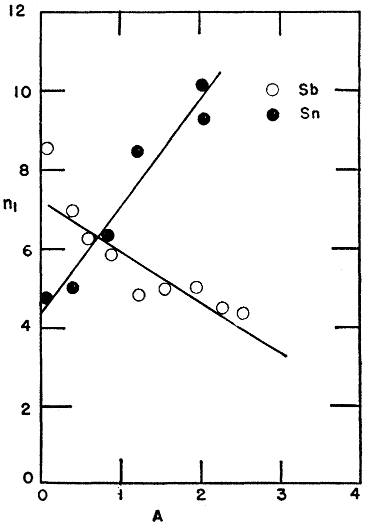

FIG. 12. Electron concentration, on arbitrary scale, versus concentration A for Sn and Sb.

that $z=3$ for Tl. This conclusion plays an important role in the subsequent discussion.

In concurrent work at this laboratory, measurements have been made of the densities of Tl-Te solutions. They indicate that the concentration of atoms $N_a=2.7 \times 10^{22}$ cm^{-3}.[9] Using Eq. (7), the match to the theoretical curve in Fig. 10, and the value $z=3$, one can deduce values for N_c and m^* in terms of the value of $\alpha(=n/n_t)$. This yields $N_c/\alpha=7.0\times 10^{20}$ cm^{-3}, and $m^*/m=3.5\alpha^{2/3}$.

IV. DISCUSSION

A. Screening of Impurities

As noted previously, the electronic behavior of Tl-Te solutions indicates that the composition Tl_2Te represents a relatively stable atomic configuration of the liquid alloy. There is also thermodynamic evidence for this. Measurements by Terpilowski and Zaleska[10] show that the excess enthalpy of mixing is negative and with a magnitude of approximately $4kT$, in the vicinity of $X \simeq 60-70$. This can be interpreted as evidence for the stability of the compound Tl_2Te.

Because of the stability of the Tl_2Te composition, one would expect excess Tl atoms or other similar elements in relatively low concentration to act as impurities in a relatively homogeneous liquid phase with composition Tl_2Te, as already assumed in the preceding analysis. But the impurity atoms, or complexes formed about them, if ionized, will form potential wells which act to localize some of the negative charge in the conduction band, and which serve to increase the screening of the potential of the ions.

Friedel has discussed in detail the screening behavior in metallic alloys.[6] The simplest approximation involves the solution of the linearized Thomas-Fermi equation. A general aspect of these solutions is that α depends on the ratio r_0/L_s, where r_0 is the radius of the spherical volume per impurity ion and L_s is the screening distance. $\alpha \sim 1$ for $r_0 \lesssim L_s$, and $\alpha \ll 1$ when r_0/L_s becomes large compared with unity. Friedel's paper presents the solution of the linearized equation, and also discusses the first-order corrections for nonlinearity. The linear approximation requires that the kinetic energy be large compared with the change in the potential energy caused by the impurity ions. This is a poor approximation in the semimetallic range of electron concentrations which occur in Tl-Te, since the Fermi energy is relatively small. However, it is possible to integrate the nonlinear equation numerically and derive information about the behavior of α without making mathematical approximations.

A more difficult problem has to do with the behavior of the dielectric constant. There is no experimental information in the case of Tl-Te about the static dielectric constant, which enters into the screening distance for semiconductors. One might guess that for Tl_2Te, which contains fairly polarizable atoms with an appreciable difference in electronegativity, it would be fairly large, probably in the range 10–20. This guess is based partly on values in the literature for physically similar solid compounds.

But one cannot rigorously describe the screening in terms of a static dielectric constant in the semimetallic range of electron concentrations. The theory for screening in this range is properly discussed in terms of many-body concepts. At the present time, this problem does not seem to have been resolved well enough to support a quantitative treatment, even if the appropriate experimental information were available. Qualitatively, one expects that the static dielectric constant enters into the screening distance properly when the plasma energy ($\epsilon_p=4\pi ne^2/m^*$) is not large compared with the kinetic energy.[11] When n is in the semimetallic range, the plasma energy exceeds the Fermi energy. As a result, the effective dielectric constant, to the extent that this is a proper concept, decreases and approaches unity at metallic concentrations.

As a result of these problems, we cannot pin down the screening distance, or even be confident that the use of the Thomas-Fermi equation is well justified. However, it will be useful for our purpose to turn the problem around as follows: We will assume that the Thomas-Fermi equation is valid in terms of a parameter which will be called the effective dielectric constant K. We will then consider whether the results in Sec. III are consistent with values of α which are to be derived from the Thomas-Fermi solutions for reasonable values of K. By doing this, the need to have accurate information about the behavior of the dielectric constant is avoided, and the Thomas-Fermi solution need not be a very accurate treatment of the screening problem. Several questions should be asked: (a) What can be said about the magnitude of α, and the corresponding implications for the Thomas-Fermi solution and the other parameters? (b) The results in Fig. 10 imply that α is nearly constant over a wider range of n_t. Is this to be expected for reasonable values of K? (c) The deduction of the valences of the doping elements assumes that α is the same for each element. Can this be justified?

A consideration of question (a) is important in setting the range for possible solutions of the Thomas-Fermi equation. Consider the mobility μ, which can be expressed in terms of the scattering distance λ_s and the de Broglie wavelength λ_d, if the value of α is known. It is convenient to calculate values of parameters, denoted with the subscript 1, on the assumption that $\alpha=1$, and express the unrestricted parameters in terms of these and α. Thus, from Sec. III, $m_1^*/m=3.3$, and $m^*=m_1^*\alpha^{2/3}$. $\mu=\mu_1/\alpha$, and one can deduce from this

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[9] Michael M. Dahl (private communication).

[10] J. Terpilowski and E. Zaleska, Roczniki Chem. **37**, 193 (1963).

[11] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963).

the average value of the product $\lambda_s\lambda_d$:

$$\mu = e\tau/m^* = (e/h)\lambda_s\lambda_d. \tag{8}$$

From the relation between the kinetic energy and the momentum,

$$\lambda_d^{-2} = 2m^*kT\mathfrak{F}_{3/2}(\xi)/h^2\mathfrak{F}_{1/2}(\xi), \tag{9}$$

so that we can deduce values of λ_{s1} and λ_{d1} from μ_1, m_1^*, and ξ. μ_1, λ_{d1}, and λ_{s1} are plotted in Fig. 13 as a function of composition in the experimental range. We see that the ratio $\lambda_{d1}/\lambda_{s1}$ decreases from 10 to 6 as X increases from 67 to 72.

Now ordinary transport theory is predicated on the assumption that $\lambda_s \gg \lambda_d$. Furthermore, Mott[12] has presented arguments for believing that electronic states, for which λ_s is relatively small, are localized and cannot be ones which participate in band conduction. They can participate in transport at most by thermally activated "hopping processes." The criterion for nonlocalized states is expressed more precisely by $k\lambda_s > 1$, where k is the wave vector, which corresponds to $\lambda_d < 2\pi\lambda_s$. This inequality is barely obeyed at $X=72$, and falls short at lower concentrations of Tl if $\alpha = 1$. Since $\lambda_s = \lambda_{s1}/\alpha^{2/3}$ and $\lambda_d = \lambda_{d1}/\alpha^{1/3}$, the above inequality yields upper limits for α, which range from $\alpha_{\max} = 0.36$ at $X=67$ to $\alpha_{\max} = 1$ at $X \geq 71$. (This result is sensitive to the choice of $\sigma_0 X \sigma_0 = 197$ instead of 182 mho/cm yielded a maximum value of 0.46 for $\alpha_{\max}$.) If α is to be nearly independent of composition, its upper limit must be set at ~ 0.5. If solutions of the Thomas-Fermi screening equation lead to a nearly constant α at reasonable values of K, for values of α below 0.5, one can conclude that the results are in reasonable accord with known theory.

[*Note added in proof.* It should be noted that the electrical conductivity depends strictly on the area of the Fermi surface and the scattering distance in the framework of transport theory with $\lambda_s \gg \lambda_d/2\pi$. Therefore, in such a case, σ would not be affected by accumulation of charge near impurity centers. This was pointed out to us by N. F. Mott, who suggested, however, that this limitation does not necessarily apply in the present situation, where $\lambda_s \sim \lambda_d/2\pi$. Thus, the explanation of our results in terms of effective removal of a fraction of the charge is hypothetical. It seems to be a way to rescue the otherwise good agreement of the experimental results with transport theory in the face of the fact that $\lambda_{s1} < \lambda_{d1}/2\pi$.]

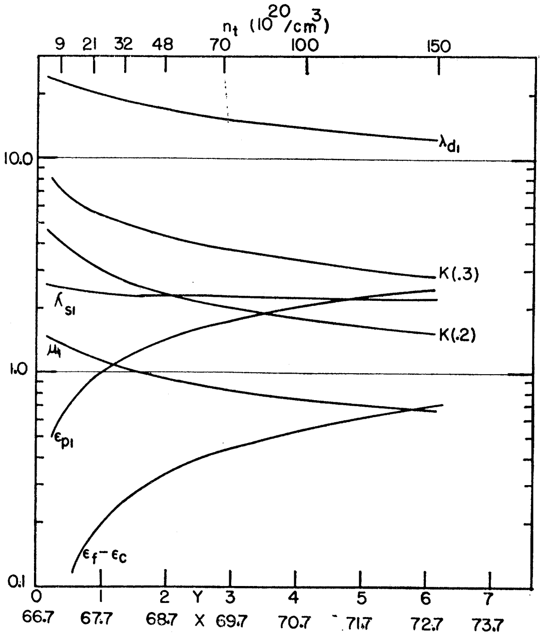

FIG. 13. Behavior of various parameters as a function of concentration. The scattering distance λ_{s1} and de Broglie wavelength λ_{d1} are in Angstrom units. The Fermi energy $\epsilon_f - \epsilon_c$ and the plasma energy ϵ_{p1} are in eV. The mobility μ_1 is in cm^2/V sec. The subscript 1 denotes value for $\alpha = 1$; the relation to α is given in the text. $K(0.2)$ and $K(0.3)$ are the computed dielectric constants for $\alpha = 0.2$ and $\alpha = 0.3$, respectively. n_t is the total electron concentration in cm^{-3}. Because of corrections of some relatively small errors, some of the curves in this figure are not in exact accord with the numerical values of parameters given in the text. The deviations are generally less than 10%.

The application of the Thomas-Fermi method to the screening of charge of an impurity leads to the equation

$$\nabla^2 V = -(4\pi e^2 N_c/K)\mathfrak{F}_{1/2}(\xi - V/kT), \tag{10}$$

where $V(r)$ is the potential energy due to the excess Tl impurity centers and K is the effective dielectric constant. This equation is solved on the assumption that there is spherical symmetry in the region about each ion out to a distance r_0, where

$$\tfrac{4}{3}\pi r_0^3 = n_I^{-1}. \tag{11}$$

n_I is the concentration of impurity ions, and is equal to n_t/z. Thus, the boundary conditions are $V=0$ and $dV/dr = 0$ at $r = r_0$. α is assumed to be equal to the fraction of the electron charge whose total energy is positive. Solutions of this nonlinear equation have been obtained by numerical methods. This work, which has some broader implications, will be reported in detail in another paper.[13] Some results of the calculations are shown in Fig. 13. The variation in K as a function of X is plotted for constant values of α equal to 0.2 and 0.3. The value $\alpha = 0.1$ leads to $K < 1$ for $X > 68.5$, which is not physically reasonable.

As noted earlier, it is expected that the dielectric susceptibility will decrease from the static value when the plasma energy ϵ_p becomes large compared with the kinetic energy, but a quantitative relationship for this behavior is unavailable. We plot ϵ_{p1} in Fig. 13 ($\epsilon_p = \epsilon_{p1}\alpha^{1/6}$).[14] It is a good deal larger than $\epsilon_f - \epsilon_c$, and

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[12] N. F. Mott, Advan. Phys. **16**, 49 (1967).

[13] M. Cutler (unpublished).

[14] It should be noted that one might also include the factor K^{-1} into ϵ_{p1}, which would decrease ϵ_{p1} and make its increase more abrupt as K decreases. However, such considerations strain the quantitative validity of our expressions.

the difference increases with X. Therefore, we might expect K to be appreciably less than the estimate of 20, and to decrease with increasing X. Thus, both plotted curves for K are reasonable. For $\alpha=0.3$, K goes from 8 to 3; and it goes from 4 to 1.5 for $\alpha=0.2$.

The remaining question is the validity of assuming the same value for α in deducing the valences z of the different doping elements. In considering the screening situation in the case of doping, it is reasonable to regard the mixture as containing two kinds of impurities: Tl ions, and ions of the third element. Then the Thomas-Fermi solution would correspond to solutions of the same boundary-value problem, Eq. (10), but with two different spherical radii to be used for Eq. (11). Both solutions require $V=0$, $dV/dr=0$ at the $r=r_0$.

Examination of the solutions of Eq. (10), in a parametrized form, shows that α is a function of ξ and K, given fixed values for m^* and T, and it does not depend explicitly on z. Now our observation that α is nearly constant as ξ (or n_I) is varied for Tl-Te means that K is changing in such a way that α does not depend on n_I. If the model suggested in the preceding paragraph is used, then this applies independently for each of the two solutions of Eq. (10) of the two kinds of spheres, with radii, say, r_A and r_B, corresponding to impurity concentrations n_A and n_B, respectively. Thus, the electron concentration corresponding to the composite solution would be

$$n=\alpha_A n_A z_A+\alpha_B n_B z_B=\alpha(n_A z_A+n_B z_B). \qquad (12)$$

This justifies the analysis in Sec. III for the effects of the doping elements.

Measurements of the Hall coefficient are normally used to determine the electron concentration. In the present case, existing information raises questions rather than answers them. The only available data for n-type Tl-Te are those of Enderby and Walsh.[15] They report $R_H=7.0\times10^{-4}$ cm^3/Coul for a sample of uncertain composition. Using their reported value of σ (800 mho/cm), we infer that $X=69.0$, and then derive $n=5.7\times10^{21}$ cm^{-3} from Eq. (7). This is smaller than $1/R_He$ by a factor of 1.6. This is not only inconsistent with our analysis of screening, which requires that $\alpha\gtrsim0.5$, but it also is inconsistent with our basic assumption that only atoms in excess of the composition Tl_2Te provide conduction-band electrons. The latter is very strongly suggested by general behavior of σ and S as a function of X and T as well as the success of our analysis in terms of band conduction. There is some question whether the conventional formula relating R_H and n is accurate in liquid semiconductors, in view of the fact that R_H is found to be negative for Tl-Te compositions where S is positive.[16] (To describe the situation fairly, it also raises a question about the use of conventional formulas for S.) In view of these questions and the limitations of the existing data, this is clearly a subject for further investigation.

B. Effect of Temperature

We have not discussed, so far, the effect of temperature on σ and S. There are two things to consider in this regard: the behavior of $\sigma(T)$ and $S(T)$ for doping by Sn and Sb, and the comparison of the theory and experiment for the other data when T is varied.

The $\sigma(T)$ curves for Sn doping (Fig. 8), considered at the high-T end, reflect an increase in electron concentration in a manner consistent with having a doubly charged donor center for each tin atom. At low T, however, electrons are apparently removed in excess of the numbers added at high T. This suggests that the tin can also form states which are acceptors. These states do not necessarily have the same atomic arrangement as the doubly ionized donor states. The electronic change which occurs at lower T may well reflect a changing chemical equilibrium. A more detailed experimental study would be needed to shed more light on what is going on.

The curves for $\sigma(T)$ as Sb is added to Tl-Te are shown in Fig. 9. As A is increased, σ decreases and also becomes more dependent on T. This is qualitatively similar to the effect of removing Tl, as would be expected for the postulated addition of acceptor states. There is a quantitative difference, however, in that the increased slope occurs at larger values of σ than it does for Tl-Te binary solutions (compare Fig. 2). Therefore, the electronic states caused by the Sb atoms are apparently varying with T, possibly in a manner similar to the Sn states. Again, a more detailed study would be required for definitive conclusions.

In Sec. III, the fitting of the experimental data to theory was carried out with isothermal data. The equations, together with the deduced constants, predict also the temperature dependence of σ and S, with, however, one further degree of freedom. The value $r=-\frac{1}{2}$, deduced above, corresponds to lattice scattering. This can arise from two different causes: the disorder of the liquid, which is independent of thermal motion, and the thermal vibrations in the liquid. The concept of thermal vibrations is valid in a liquid over a major part of wave-vector space.[17] In the former case, τ_0 in Eq. (1) is independent of T, and in the latter τ_0 is inversely proportional to T. In Fig. 2, we show theoretical curves for $\sigma(T)$ assuming that τ_0 is independent of T. They agree well in slope with the experimental curves at higher electron concentrations, indicating that the intrinsic disorder makes the major contribution to scattering. At lower electron concentrations, the experimental curves for σ increase with increasing T,

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[15] J. E. Enderby and L. Walsh, Phil. Mag. 14, 991 (1966).

[16] James M. Donally, and M. Cutler, Bull. Am. Phys. Soc. 12, 911 (1967).

[17] A. I. Gubanov, *Quantum Electron Theory of Amorphous Conductors* (Consultants Bureau Enterprises, Inc., New York, 1965), p. 70.

in contrast to the slightly decreasing theoretical curves. This can be ascribed to thermal excitation of extra carriers at higher T and near-intrinsic compositions.

It is interesting to note that the earlier study[2] of *p*-type compositions also led to an indication that there was "lattice" scattering, but it was the phonon type of scattering. It seems possible to provide a plausible explanation for the two apparently inconsistent results. It is likely that the valence band is associated with largely covalent bonds in Tl_2Te, and compounds derived from it on adding Te. These are perhaps arranged in partial chains, like a molten organic polymer. The charge distribution for holes would tend to lie along these bonds. Therefore the holes would not see the disorder of the molecular chains, but would be quite sensitive to thermal vibrations. On the other hand, electrons are probably in antibonding states, whose spatial distribution would not be so strongly confined to the molecular structure. Therefore, they would see the disorder more, and be less sensitive to the thermal vibrations.

The theoretical curves for $S(T)$ are shown in Fig. 3 in addition to the experimental curves. The former vary almost linearly with T, as expected for semimetallic transport. The experimental curves agree fairly well at large n, but show a considerable decrease in the magnitude of S with increasing T at high T and low n. This can be caused by excitation of extra carriers. They may well be due to thermal excitation of electron-hole pairs at near intrinsic compositions. There is also a possibility that a significant contribution may arise from thermal excitation of electrons in localized states. This also may account for the small difference in slopes for $\sigma(T)$ (Fig. 2) at similar values of X and T. A more precise study of the effect of T on S and σ may indicate whether the latter possibility is a likely one.

V. CONCLUSIONS

The results of our analysis show that the behavior of the electrical conductivity and the Seebeck coefficient, as a function of composition and temperature, can be interpreted very well in the framework of the concepts and theoretical equations of conventional theory for highly doped semiconductors or semimetals. In view of the questionable validity of some of the assumptions of this theory, this apparent agreement should not be regarded as proof that the theory is correct in detail, but rather as an indication that it contains many elements which are valid in some broad sense. The exact situation will not be known until a rigorous development of theory is obtained which is appropriate for disordered systems such as Tl-Te, and which is transparent enough so that detailed comparison with experiment is possible. The present work may help to provide clues for the construction of such a theory.

Given this situation, the quantitative conclusions which were extracted by our analysis have a somewhat shaky foundation. Nonetheless, the considerable dovetailing of various parts of the results tends to support their validity. The main conclusions are, in summary, as follows: The addition of excess Tl to the Tl_2Te creates donor centers with a charge of $+3e$. Because of partial trapping of the screening electron cloud only a small fraction α of these electrons moves freely and participates in transport.[18] This fraction is nearly constant over the experimental range of compositions. The effect of adding small amounts of a third element is the same as adding Tl, except that the charge of the donor or acceptor centers is different. The deduced valences correspond well with the common chemical behavior for the elements studied.

The dependence of σ on the electron concentration indicates that the main scattering mechanism is the intrinsic (nonthermal) disorder of the liquid. This is in contrast with the scattering mechanism for holes, whose transport is dominated by phonon scattering.[19] An explanation for this has been advanced in terms of the atomic and electronic structure of the liquid.

Analysis of the screening behavior and consideration of the transport behavior permit assignment of numerical values to some of the parameters within a fairly broad range. The fraction α of free charge lies between 0.15 and 0.5, which implies that the effective dielectric constant K is in the range 1 to 10, and that the effective-mass ratio m^*/m is in the range 1 to 2.[18]

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[18] See the note added in proof in Sec. IV A.

[19] Note that deductions about the scattering mechanism through the value of r in the standard transport equations depend on the assumption that the density of states has a square-root dependence on the energy distance from the band edge. This point is discussed extensively in Ref. 2.