Temperature-dependent conductivity of metallic doped semiconductors

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We have analyzed the temperature dependence of the electrical conductivity of a series of metallic samples of Ge:Sb in the temperature range 10 mK to ¹ K. We find a temperature dependence that is consistent with a sum of the behaviors predicted by Coulomb interactions and localization theories. The observed density dependence of the Coulomb contribution is consistent with theory but its magnitude differs by a factor of up to 4 if intervalley scattering is neglected. With our fitting procedure the dominant inelastic scattering process is electron-electron with a density dependence in reasonable agreement with theory. The magnitude of this scattering is enhanced by a factor of \sim 2 over the prediction for weak scattering but is much too small to be properly described by existing strong-scattering theories.

The transport properties of doped semiconductors at low temperatures near a metal-insulator transition have been studied previously.¹⁻⁶ A steep decrease was found³ in the resistivity with decreasing temperature of metallic samples of Ge:Sb. The temperature dependence seemed to be $ln(T)$ between 0.1 and 1 K, with a magnitude that became larger as the donor concentration was reduced toward n_c , the density of the metal-insulator transition. These results, together with the observed negative magnetoresistance, were compared with effects expected to arise from s-d interactions. Part of the positive magnetoresistance observed at lower temperatures was explained within the framework of the Kondo effect.⁴ Measurements of the magnetic susceptibility⁷⁻⁹ and the specific heat¹⁰ of similar semiconductors suggested the existence of localized magnetic moments near n_c . However, these discussions were qualitative because adjustable parameters were unavoidably involved.

Recently there has been progress in the theory of disordered materials from two points of view: the effects of Anderson localization¹¹⁻¹⁶ and the effects of electron-electron interactions. ¹⁷⁻²⁶ These theories predict behaviors different from those of periodic systems. In one and two dimensions, these theories can explain the T variation of the conductivity.^{$27,28$} In this paper, we compare these

new theories with the behavior of three-dimensional $(3D)$ doped Ge and with previous results⁵ in $Si:$ P and other 3D systems.²⁹ Within the framework of localization, we shall utilize results related to the theory of negative magnetoresistance developed by Kawabata.¹⁵ As we show below, the scaling theory of localization, predicts a positive correction to the $T=0$ K conductivity, $\sigma(0)$, proportional to T (if weak²³ electron-electron scattering dominates) as opposed to the behavior in periodic systems of a negative term varying as T^2 (or higher powers of T for phonon scattering). An alternative estimate based on localization²⁹ also yields a positive correction, but of the form $T^{1/3}$. From a different point of view, theories¹⁷⁻¹⁹ considering the Coulomb interactions among electrons in a random system predict a temperature correction to $\sigma(0)$ of the form $T^{1/2}$, with a prefactor that can change sign as the size of the screening length varies.

Experimenally, the T variations in Si:P have been analyzed^{5,6} assuming only a contribution from Coulomb interactions. A negative temperature correction was found well above n_c with an exponent in the range $0.2-0.7$, consistent with the prediction of a negative $T^{1/2}$ term. The size of the effect was of the right order, but there remains a substantial theoretical uncertainty related to inter-

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valley scattering. This "cusp" was found to grow as n was lowered toward n_c and to change sign very near n_c in agreement with the expected trend.

In contrast to the negative temperature correction in Si:P, studies of amorphous $Ge_{1-x}Au_x$ alloys showed²⁹ a positive correction to $\sigma(0)$ for temperatures down to \sim 1 K. The temperature dependence was found to be consistent with $T^{1/3}$, although the results appear to be consistent with $T^{1/2}$ also.

The temperature correction to $\sigma(0)$ in Ge:Sb, which seemed to vary³ as $ln(T)$, is qualitatively similar to that in Si:P, i.e., the temperature deriva tive $d\sigma/dT$ becomes large as T goes to zero, and the size of the correction grows as n is lowered toward n_c . Therefore, we have reexamined this effect in terms of the new theories. A major difference from the previous analyses of Ge:Sb and Si:P is that here we include both $+ T$ and $-T^{1/2}$ types of contributions. With this procedure we can describe the data over a wider T region than earlier fits in Ge:Sb. We also obtain the first analysis of the magnitude of the localization contribution.

The temperature dependence of the conductivity $\sigma(T)$ of a series of samples of Ge:Sb is shown in Fig. 1. The samples we have measured are characterized by net donor density n , zero-temperature conductivity $\sigma(0)$, and compensation ratio K_0 as given in Table I. In Ge:Sb, the critical density, $n_e = 1.5 \times 10^{17}$ cm⁻³, is considerably lower than in the other systems mentioned above. The values of σ (0) range from near Mott's σ_{\min} , 17 (Ω cm)⁻¹ (Ref. 2) [where $\sigma(T)$ increases with increasing T] to $\sigma(0) \approx 16\sigma_{\min}$ (where metallic T dependence is observed). In the "metallic" cases in Fig. ¹ a small, sharp rise in $\sigma(T)$ can be seen as $T\rightarrow 0$ and inverted behavior seen near σ_{\min} . The data for $n = 4.8 \times 10^{17}$ cm⁻³ (because of the larger K_0) fall near that for $n = 3.3 \times 10^{17}$ cm⁻³ and are therefore not shown in Fig. 1. Qualitatively, the magnitude of K^0 does not change the temperature dependence radically.

In Fig. 1, the solid line through the data indicates the region over which the results can be reasonably described by a $T^{1/2}$ term (e.g., 10 - 150 mK for $n = 3.3 \times 10^{17}$ cm⁻³). The dashed line represents a guide to the eye (at higher T) or our extrapolation to $T=0$ K. It is important to note that the region over which the $T^{1/2}$ fit can be made is restricted to much lower temperatures in Ge:Sb than previously observed^{5,6} in Si:P. This restricted region introduces substantial systematic uncertainty into our analysis and may arise because of a larger contribution from localization effects.

FIG. 1. Conductivity of a series of samples of Ge:Sb as a function of temperature. The curves are labeled with the net donor density n . In each case the temperature correction to $\sigma(0)$ can be seen to be of the form T^{β} with β < 1. The magnitude of this "cusplike" contribution grows as n decreases (toward the critical density $n_c = 1.5 \times 10^{17}$ cm⁻³) and reverses sign where $\sigma(0)$ is near Mott's σ_{\min} . The results of our analysis of these curves are illustrated in Figs. $2-5$. The solid curves through the data are fitted to the form $T^{1/2}$, the dashed curves at lower T are extrapolations of this same form, and the dashed curves at higher T are guides to the eye.

The sample near σ_{\min} , however, can be fit with only a $T^{1/2}$ correcion over the entire region shown in Fig. 1.

Figure 2 shows the temperature dependence of

TABLE I. The Ge:Sb crystals studied in Figs. $1-5$ have the Sb densities n, $T=0$ K conductivities $\sigma(0)$, and compensation ratios K_0 given here.

$n (10^{17} cm^{-3})$ $(+5%)$	$\sigma(0)$ $(\Omega^{-1}$ cm ⁻¹) $(+5%)$	K_0 (%) $(+10\%)$
6.4	114	25
4.8	65	25
3.3	67	
2.6	39.5	$\leqslant 5$ 20
2.05	31.7	
1.6	7.6	≤ 5 ≤ 5

FIG. 2. Detailed analysis of a representative sample showing $\sigma(T)$ with an expanded scale as a function of T (linear in $T^{1/2}$). The dashed line is the simplest fit considering only the negative $T^{1/2}$ behavior predicted by Coulomb interactions theories. The variation of the slope of this line for other samples is shown in Fig. 3. The dashed-dotted lines are contributions of the same $T^{1/2}$ form and of the form T expected from weak electron-electron scattering within localization theory. The sum of the dashed-dotted curves is the solid line which fits a wider range of T than the $T^{1/2}$ curve alone. The variation of the magnitude of the contribution $\propto T$ for all samples is summarized in Fig. 4.

the electrical conductivity $\sigma(T)$ on an expanded scale for a sample with compensation $K_0 \leq 5\%$. The data, at concentration $n = 3.3 \times 10^{17}$ cm⁻³, have a zero-temperature conductivity $\sigma(0)$ $\sim 10\sigma_{\min}$, so that they represent the behavior of a reasonably good metal. This sample shows behavior representative of all five "metal-like" samples we have measured.

Three fits have been made to the data for each sample and two of these we illustrate in Fig. 2. All fits were of the general form suggested by theories of Coulomb interactions and localization effects in 3D random systems,

$$
\sigma(T) = \sigma(0) + mT^{\beta} + BT \tag{1}
$$

Coulomb interaction theory¹⁷⁻²⁶ gives $\beta = \frac{1}{2}$ and

$$
m = S_0 \frac{e^2}{2\pi^2 \hbar} 0.46A \left[\frac{k_B}{D\hbar} \right]^{1/2}, \qquad (2)
$$

where D is the diffusion constant, and

$$
S_0 = \frac{1}{\nu} \sum_{i=1}^{\nu} m^* \left(\frac{\sin^2 \theta_i}{m_t} + \frac{\cos^2 \theta_i}{m_l} \right), \qquad (3)
$$

 θ_i being the angle between the current and the axis of the spheroidal energy surface of the ith valley and ν the number of the valleys. The contribution to A from hole-particle scattering is given³¹ by

$$
A_{hp} = \frac{4}{3} - 2F\delta \tag{4}
$$

where

r

$$
F = \frac{vm^*}{2\pi^2 k_F \hbar^2} \int_0^{2k_F} v(p)p \, dp \,, \tag{5a}
$$

 $v(p)$ being the potential of electron-electron interaction. In the right side of Eq. (4), the first term is the contribution from the exchange correction, the second is that from the Hartree correction.

The parameter δ is introduced to take into account^{25,26,31} the valley degeneracy ν (ν = 4 for Ge and 6 for Si), the valley anisotropy and the intervalley scattering. We estimate

$$
\delta = \begin{cases} 1 & (\text{Ge}) \\ 2 & (\text{Si}) \end{cases} \tag{5b}
$$

based on the number of valleys with symmetric anisotropy. Following a more detailed analysis, Bhatt and Lee 31 find

$$
\delta = \begin{bmatrix}\nv \text{ (no intervalley scattering)} \\
1 / v \text{ (isotropic values)} \\
1 \text{ (anisotropic Ge)} \\
\frac{1}{2} \text{ (anisotropic Si)}\n\end{bmatrix}\n\begin{bmatrix}\n\text{large intervalley} \\
\text{scattering}\n\end{bmatrix}
$$
\n(5c)

and intermediate results for scattering between the large and small limits.

We have obtained the contribution to A from the particle-particle scattering by converting the results for 2D by Fukuyama²¹ to 3D and we find

$$
A_{pp} = \begin{cases} -F & (\text{Ge}) \\ -3F & (\text{Si}), \end{cases}
$$
 (6)

which we add to A_{hn} . For $v(p)$, we assume a screened Coulomb interaction. Within the Thomas-Fermi approximation F is given^{5,31} by

$$
F = \frac{1}{x} \ln(1+x) ,
$$

where

$$
x = (2k_F/\kappa)^2
$$

and hence F reduces to 1 when $x \rightarrow 0$. For the experimental conditions in Ge:Sb, x is not small and

 (7)

the deviation of F from 1 can be considerable. However, numerical calculations indicate that, if we apply the random-phase-approximation dielectric function, F is close to 1 (within 5%) for the electron densities of most of our samples.

The effect of anisotropy on A has been ignored since we estimate this effect to be less than 15% in all our Ge:Sb samples. Nevertheless, the anisotropy of the effective mass tensor is important for S_0 , since $S_0 = 1.85$ when the current is along (110) and $S_0 = 1$ if the anisotropy is neglected. (For Si, S_0 = 1.26 irrespective of the direcion of the current.) We use

$$
\sigma(0) = 2S_0 v e^2 DN(0) \tag{8}
$$

to determine D , where the density of states $N(0)=m*k_F/2\pi^2\hbar^2$.

The linear term BT in Eq. (1) arises within the localization theory¹² if we assume that the energy relaxation time τ_{ϵ} is of the form

$$
1/\tau_{\epsilon} = cT^2 \,, \tag{9}
$$

where the constants B and c are related by

$$
B = S_0 \nu \frac{e^2}{2\pi^2 \hbar} \left(\frac{c}{D}\right)^{1/2}.
$$
 (10)

For this case, the constant c can be calculated if we assume the energy relaxation to be due to electron-electron scattering, for which τ_{ϵ} is given³² by

$$
\frac{\hbar}{\tau_{\epsilon}} = 4 \left[\frac{\pi}{4} \right]^3 \frac{e^2 k_F \gamma}{\sqrt{3} \hbar \epsilon} \left[\frac{k_B T}{E_F} \right]^2, \qquad (11)
$$

where ϵ is the dielectric constant and

$$
\gamma\!=\!E_F/\hslash\omega_p
$$

and

$$
\omega_p = \left[\frac{4\pi e^2 n}{m^* \epsilon}\right]^{1/2}.
$$

(12)

Then we find from Eqs. $(10) - (12)$ that we can define a constant c' , independent of n .

$$
c' \equiv cn^{-5/6} = 4 \left[\frac{\pi}{4} \right]^3 \left[\frac{1}{3\pi} \right]^{1/2} \left[\frac{\nu}{3\pi^2} \right]^{1/3} \frac{m^* k_B^2}{\hbar^3 \sqrt{a_B}}
$$

= 0.17 × 10¹⁰ K⁻² sec⁻¹ (Ge)
= 0.42 × 10¹⁰ K⁻² sec⁻¹ (Si), (13)

where the Bohr radius $a_B = \hbar^2 \epsilon / m^* e^2$ and the car-

rier density \tilde{n} is in units of 10^{18} cm⁻³.

The fit shown by the dashed line in Fig. 2 is that suggested by the analysis considering only Coulomb interaction effects and so has fixed parameters, as defined by Eq. (1):

$$
\beta = \frac{1}{2}, \quad B = 0 \tag{14}
$$

Because we wish to emphasize that this $T^{1/2}$ contribution alone provides a reasonable description of our results in the limit $T\rightarrow 0$ K, we have plotted the results versus $T^{1/2}$ in Fig. 2. (The T scale is linear in $T^{1/2}$.) The good fit is restricted, however, to $T < 150$ mK. We shall discuss the magnitude of the fitted values of m below and in Fig. 3. The values of $\sigma(0)$ have been discussed previously by Thomas et al.³³ The T region to which the fit here is restricted is smaller than that in Si:P partly because both the electronic and lattice characteristic energies are lower in Ge than in Si.

The fit shown by the solid line in Fig. 2 is an at-

FIG. 3. Variation of the magnitude of the $T^{1/2}$ corrections to $\sigma(0)$ as defined by fits using the equation in the inset. The results for both Ge:Sb and Si:P on a logarithmic scale of n are shown along with the critical densities n_c (dashed vertical lines). The solid curves are the predictions of the Coulomb interaction theory with n dependence as evaluated in the text and fitted values of A defined by Eq. (2). The fitted A's differ from the theoretical values based on Eqs. (4) – (6) by 2.6 in Ge:Sb and by $\sim \frac{1}{4}$ in Si:P.

tempt to include approximately localization effects arising from electron-electron scattering by considering finite values of B in Eq. (1).

$$
\beta = \frac{1}{2}, \ \ B \neq 0 \ . \tag{15}
$$

The fit in this case extends to T about a factor of 4 higher, but is still restricted to $T < 0.5$ K. The fitted values of $\sigma(0)$ are not appreciably affected by the choice of B , but the values of m are somewhat larger. The two contributions which are assumed to obtain the solid line are shown by the dasheddotted lines in Fig. 2. The prefactors m and B resulting from this analysis are summarized for all samples in Figs. 3 and 4.

In the third type of fit to the data, we have used a variable value of β and set $B=0$. The value of β tends to be smaller if a larger T region is included, as can be seen qualitatively in Fig. 2, but the fit becomes worse. The values of $\sigma(0)$ are again not appreciably changed. The results for these fitted exponents are shown in Fig. 5. The points represent the best fit values of β for the T regions indicated by solid lines in Fig. 1, while the error bars show both statistical errors and the variation of β values when the data at higher T are included. If the T region above 500 mK is included, a fit such as this with only one term is not satisfactory (except for $\tilde{n} = 0.16$).

Figure 3 summarizes our results based on the first type of fit, using Eqs. (1) , (2) , and (14) . The magnitude of the low-temperature conductivity correction m is plotted on a linear scale as a function of n on a logarithmic scale. We have shown

FIG. 4. Variation of the size of the linear T term as defined by the inset equation as a function of density. The solid curve is a fit to the data using a constant c' , defined by Eq. (13), that is larger than theory by a factor \sim 2.

FIG. 5. Best fit exponents as defined by the inset equation as a function of density. Horizontal line is $\beta = \frac{1}{2}$

the results for Si:P for comparison. The values of density at the metal-insulator transition are indicated by dashed lines and arrows labeled n_c and have values $n_c = 1.55 \times 10^{17}$ cm⁻³ for Ge:Sb and $n_c = 3.74 \times 10^{18}$ cm⁻³ for Si:P. The comparison shown in this figure indicates that the size of the effect is larger in Ge than in Si.

For both materials, a change in sign of m occurs near n_c as can be expected qualitatively⁵ if the screening wave vector κ tends to diverge³⁴ near n_c . The expected size of the $T^{1/2}$ term in Si:P compared to Ge:Sb is also related to the value of κ compared to the Fermi wave vector k_F . The Coulomb interaction theories predict in general an increase in $-m$ with decreasing k_F/κ . To compare these theories with our results, we have used free-electron formulas for k_F and κ ,

$$
k_F = (3\pi^2 n / \nu)^{1/3} \tag{16}
$$

$$
\kappa = 12\pi n e^2 m^* / (\epsilon h^2 k_F^2) \ . \tag{17}
$$

In these equations, we have used valley degeneracy ν , effective mass m^* , and dielectric constant ϵ values given by $(v,m^*, \epsilon) = (4,0.22m_\epsilon, 15.4)$ for Ge and $(6,0.33m_e, 11.4)$ for Si. As a result of the difference in these parameters, the value of $x = (2k_F/\kappa)^2$ which enters the theories is 0.568 $\tilde{n}^{1/3}$ for Ge and $0.162\tilde{n}^{1/3}$ for Si, where \tilde{n} is in units of 10^{18} cm⁻³. Because of this larger prefactor, Ge:Sb has larger values of x, and so smaller values of $-m$ are expected theoretically for the same values of D, if intervalley scattering is neglected.³¹ The theoretical functional dependence of m on n is given by the solid lines shown in Fig.3; the curve is fitted to experiment using the constant A in Eq. (2) as a parameter. The fit is satisfactory indicating a

consistent n dependence between theory and experiment. However, the observation of larger values of $-m$ in Ge:Sb than in Si:P contradicts the theoretical expectation. The fitted value of A in Si:P is about $\frac{1}{4}$ of the theory given above in Eqs. (1)–(8) and in Ge:Sb is about 2.5 times bigger than this theory. We interpret this disagreement as indicating that the intervalley scattering should be included. Rosenbaum et al , $\stackrel{6}{\ }$ have reached the same conclusion based on magnetoresistance measurements in Si:P.

Figure 4, together with Fig. 3, summarizes our results using the second type of fit, illustrated in Fig. 2 by the dashed-dot lines. In this case we use Eq. 1 and $\beta = \frac{1}{2}$ as indicated in the inset to Fig. 4, but also include the term BT . The resulting values of $-m$ are larger by about 4 (Ω cm $K^{1/2}$)⁻¹ than those shown in Fig. 3 and the values of $\sigma(0)$ are increased by ≤ 1 (Ω cm)⁻¹. Both these changes in the fit can be seen in Fig. 2. The error bars in Fig. 3 have their upper limit determined by $-m$ from this method and their lower limit set symmetrically. The observed magnitude of the positive linear term, given by our values of B , increases with decreasing *n* as shown in Fig. 4. Near n_c , however, the value of B drops to zero within the accuracy of our fit. The systematic uncertainty in our value of B is subject to the same factors discussed above for m , but it is larger because of the additional fitting parameter. We estimate the uncertainty to be about 20%. The solid line through the data in Fig. 5 is a fit using c' , in Eq. (13), as a parameter; the dashed line is a guide to the eye. Our value of c' is $(0.3\pm0.1)\times10^{10}$, larger by only a factor of about 2 than the calculation of Quinn and Ferrell³² of $c' = 0.17 \times 10^{10} \text{ K}^{-2} \text{sec}^{-1}$.

The effects of disorder on τ_{ϵ} have been discussed by Schmidt³⁵ and also by Altshuler and Aronov³⁶ and by Abrahams et $al.^{23}$. They have found that the $1/\tau_{\epsilon}$ due to electron-electron scattering is enhanced because of disorder and is proportional to $T^{3/2}$. This leads to a temperature correction to

 $\sigma(0)$ of the form

$(S_0\nu/4\pi^2)(e^2/h\sqrt{I/k_F})(\hslash/m^*D)^{3/4}(T/E_F)^{3/4}$,

for small T/E_F as in our experiment. Using freeelectron formulas for the mean free path $l = \hbar k_F \sigma(0)/ne^2$, for the diffusion coefficient $m^*D/\hbar=k_Fl/3$, and for k_F and E_F , we have evaluated this contribution for Ge:Sb. We find a conductivity that is an order of magnitude larger than experiment and therefore we have not used this formulation in our analysis above. However, the fact that our analysis of the experiment gives a larger value of $1/\tau_{\epsilon}$ than the theory may indicate some effect of disorder on τ_{ϵ} .

Figure 5 shows the results of our third type of fit. Here we use $B = 0$, and β as a variable. In this case both m and $\sigma(0)$ are only slightly changed from the analysis using $\beta = \frac{1}{2}$. As seen in Fig. 5, the best fit values of β are consistent with $\frac{1}{2}$ (in the low-T limit discussed above) except for the point very near n_c where a slightly smaller value occurs. The solid line through $\beta = \frac{1}{2}$ is the prediction of the Coulomb interactions theories and should be valid for $k_F l \gg 1$. We calculate $k_F l = 0.012\sigma(0)/\tilde{n}^{1/3}$ using free-electron theory, with \tilde{n} in units of 10¹⁸ cm⁻³. Using this equation, $k_F l = 1$ falls at slightly higher *n* than the sample $n = 2.6 \times 10^{17}$ cm⁻³, so the theory line is dashed below this point.

In conclusion, we have compared the temperature dependence of the conductivity of Ge:Sb with recent theories of disordered systems. The observed behavior is consistent with additive contributions from both Coulomb interactions and localization with electron-electron scattering.

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