recent piezo-optical studies of the Bi bound exciton lines in GaP.[10] The relative intensity of the B line increases rapidly with magnetic field because of mixing of magnetic substates of the $J=1$ and $J=2$ exciton states by the magnetic field. The anisotropic hole g factor L is negative for this bound exciton state. Positive values of L have been obtained for other systems in which the hole is bound by Coulomb forces, unlike the Bi bound exciton. We identify a previously unreported (0.28 ± 0.02)-meV splitting of the B line in zero magnetic field with a crystal-field interaction which splits the $J=2$ exciton state into Γ_3 and Γ_4 states, the latter lying lower.

ACKNOWLEDGMENTS

The authors are grateful to J. L. Merz for the provision of laboratory facilities for these experiments. We are also indebted to G. Kaminsky and E. A. Sadowski for technical assistance.

PHYSICAL REVIEW VOLUME 185, NUMBER 3 15 SEPTEMBER 1969

Temperature Dependence of the Resistivity of Degenerately Doped Semiconductors at Low Temperatures

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(Received 20 March 1969)

The temperature dependence of the resistivity ρ has been calculated, assuming Brooks-Herring scattering, for a degenerately doped semiconductor having ν valleys in the conduction band, all with the same isotropic effective mass m^*. For temperatures well below the degeneracy temperature T_D, we derive the expression $\Delta\rho/\rho_0=\gamma(T/T_D)^2$, where ρ_0 is the resistivity at $T=0$, and γ is a function only of the dimensionless parameter $a_0k_0/\nu^{4/3}$. Here k_0 is the Fermi wave number if all the electrons were in a single valley, and a_0 is the first Bohr radius in the material. For $\nu=1$, γ is always negative for degenerate doping and the values obtained are in quantitative agreement with available experimental data. For $\nu>1$, γ may be either positive or negative, but for all Si and Ge data available, its magnitude is smaller than that obtained from experimental results, suggesting the existence of a contribution to the resistivity due to intervalley electron-electron scattering.

I. INTRODUCTION

It is well known that the activation energy, i.e., the ionization energy of an electron bound to a donor in a semiconductor, decreases as the doping density increases[1] because of the electron-electron repulsion.[2,3] For sufficiently high donor concentrations, the activation energy vanishes and the donor electrons are free to move in the conduction band.[1-4] These heavily doped materials are known as degenerately doped semiconductors (d.d.s.) when $T\ll T_D$, where T_D is the degeneracy temperature. They have certain features in common with metals, i.e., the electrons in the conduction band obey Fermi-Dirac statistics, the distribution being degenerate for $T\ll T_D$, and the Hall constant is independent of the temperature. However, T_D for semiconductors is always much lower than those for metals, typical values for T_D being between a few tens of degrees and a few thousand degrees Kelvin for semiconductors.

There has been considerable experimental and theoretical interest in the temperature dependence of the resistivity of d.d.s. Early data on silicon[1,5-8] and germanium[9-14] showed that the resistivity is essentially constant at very low temperatures, then rises as the temperature increases, and finally becomes linear in T at high temperatures—behavior which is similar to that of an impure metal. The temperature-dependent part of the resistivity is, however, too large to be accounted for by phonon scattering alone.[7,14] Koenig[14] has argued that this behavior cannot be understood in terms of scattering from screened ionized impurity atoms, because such scattering decreases as the incident

[1] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).
[2] S. P. Li, W. F. Love, and S. C. Miller, Phys. Rev. **162**, 728 (1967).
[3] J. B. Krieger, Phys. Rev. **178**, 1337 (1969).
[4] N. F. Mott, Phil. Mag. **6**, 287 (1961); M. N. Alexander and D. F. Holcond, Rev. Mod. Phys. **40**, 815 (1968).
[5] F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).
[6] R. O. Carlson, Phys. Rev. **100**, 1075 (1955).
[7] P. W. Chapman, O. N. Tufte, J. D. Zook, and D. Long, J. Appl. Phys. **34**, 3291 (1964).
[8] D. Long, J. D. Zook, P. W. Chapman, and O. N. Tufte, Solid State Commun. **2**, 191 (1964).
[9] Y. Furukawa, J. Phys. Soc. Japan **16**, 687 (1961).
[10] O. A. Golikova, B. Ya. Moizhes, and L. S. Stil'bans, Fiz. Tverd. Tela **3**, 3105 (1961) [English transl.: Soviet Phys.—Solid State **3**, 2259 (1962)].
[11] V. I. Fistul', M. I. Iglitsyn, and E. M. Omel'yanovskii, Fiz. Tverd. Tela **4**, 1065 (1961) [English transl.: Soviet Phys.—Solid State **4**, 784 (1962)].
[12] W. Sasaki and R. De Bruyn Ouboter, Physica **27**, 877 (1961).
[13] W. G. Spitzer, F. A. Trumbore, and R. A. Logan, J. Appl. Phys. **32**, 1822 (1961).
[14] S. H. Koenig, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 5.

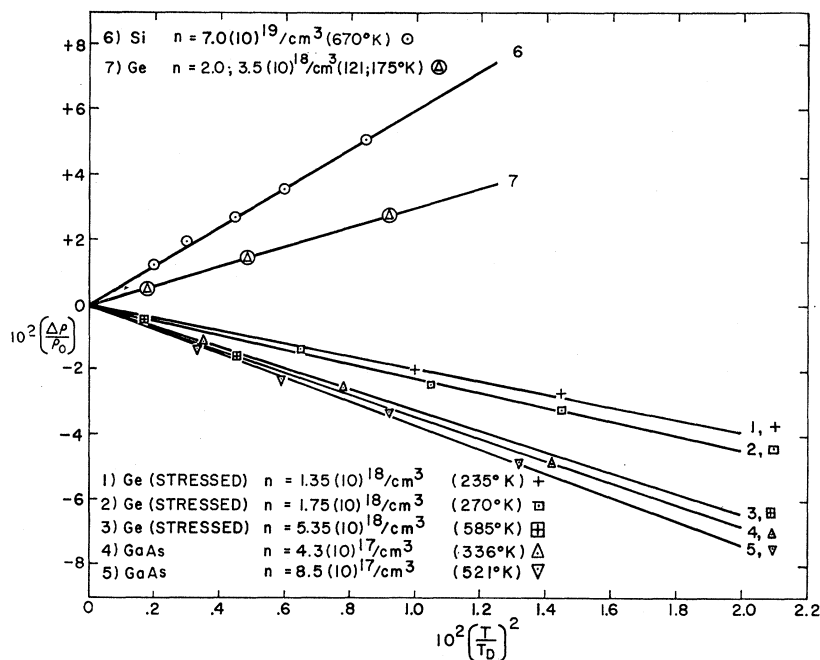

FIG. 1. Fractional resistivity increment versus $(T/T_D)^2$. Only a few of the data points are shown. The GaAs samples are tellurium-doped, all others are arsenic-doped. The numbers in parentheses represent the degeneracy temperature T_D.

energy of the electrons is increased. Instead, he has proposed that a shielded impurity acts as a dipole when the center of the screening charge is displaced from the impurity ion by thermal vibrations. This mechanism, dipole scattering, gives a positive temperature coefficient. More recently, however, Katz[15] has found that ρ decreases with increasing temperature when the electrons in germanium are shifted into a single conduction-band valley by the application of stress. Thus the dipole scattering model must be abandoned since it predicts a positive temperature coefficient in this case also.

Morgan[16] has proposed that intervalley electron-electron scattering could account for the positive temperature coefficient in the many-valley case—for example, unstressed Ge and Si. Such scattering will make a positive contribution to ρ_0 proportional to T^2 provided the valleys are anisotropic.[17] The T^2 dependence follows from the fact that conservation of energy and the exclusion principle require that both electrons occupy states in the thermal layer of the Fermi surface. Furthermore, for a single valley or many equivalent isotropic valleys, conservation of electron quasimomentum in electron-electron scattering is equivalent to conservation of the sum of the electron velocities, and as a result the contribution to the resistivity will be negligible. It is for this reason that *e-e* scattering in transition metals makes no contribution to ρ through $O(T^2)$ if both *s* and *d* electrons have the same isotropic effective mass.[18]

The T^2 dependence in the many-valley case has recently received some experimental support for arsenic-doped germanium,[19] but a realistic calculation must include the temperature dependence of the shielded ion scattering which, for $T \ll T_D$, will also make a contribution to ρ proportional to T^2. This follows from the fact that, for electrons obeying degenerate Fermi statistics, the Fermi energy and the Thomas-Fermi inverse screening length change by $O(T^2)$ as the temperature is raised from 0°K, and the Sommerfeld expansion of the conductivity integral is an expansion in powers of T^2. These terms lead to a fractional change in the conductivity proportional to $(T/T_D)^2$. These contributions are always unobservable for metals because $T_D \approx 10^4$–10^5°K, whereas the smallness of T_D for d.d.s. makes these terms significant here. These considerations have led us to plot the fractional change in ρ versus $(T/T_D)^2$ for eight d.d.s.[7,15,19,20] Figure 1 shows that not only in many-valley semiconductors, but also in the single-valley materials (GaAs and stressed Ge), $\Delta\rho$ follows a T^2 dependence to a good approximation, provided $T \ll T_D$ and T is low enough that ionized impurity scattering is predominant over lattice scattering.

The calculation of the temperature dependence of ρ due to electrons scattered from screened ions (Brooks-Herring scattering[21]) has been given by Mansfield[22] for arbitrary electron statistics, together with the effect of lattice scattering. Because of the attempted generality of his calculation, it is not clear what scaling laws, if

[15] M. J. Katz, Phys. Rev. **140**, 1323 (1965).
[16] T. N. Morgan, Bull. Am. Phys. Soc. **8**, 224 (1963).
[17] P. J. Price and J. B. Krieger, Bull. Am. Phys. Soc. **11**, 400 (1966).
[18] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960), p. 415.
[19] M. J. Katz, S. Koenig, and A. Lopez, Phys. Rev. Letters **15**, 828 (1965).
[20] The GaAs and Si data are due to D. Long (private communication).
[21] H. Brooks, Advan. Electron. Electron Phys. **7**, 128 (1955).
[22] R. Mansfield, Proc. Phys. Soc. (London) **69B**, 76 (1956).

any, are operative which describe ρ as a function of T. Such scaling laws are known to exist for obtaining the corrections to the Born approximation when treating Brooks-Herring scattering for degenerate statistics.[23]

We have calculated the low-temperature resistivity due to electron scattering from screened ionized impurity atoms for a d.d.s. having static dielectric constant κ and ν conduction-band valleys each having isotropic mass m^*. We find that the fractional change in the resistivity is given by

$$\Delta\rho/\rho_0=\gamma(T/T_D)^2.$$

Here γ is a universal function of $a_0k_0/\nu^{4/3}$, where $a_0=\hbar^2\kappa/m^*e^2$ is the radius of the first Bohr orbit in the material and k_0 is the Fermi wave number for the case where all the electrons are in a single valley. The results of the calculation are in good agreement with experimental data for the single-valley case, but underestimate the observed γ for the many-valley anisotropic case because of the neglect of intervalley electron-electron scattering in this model. In performing the calculation we have assumed that the semiconductor is so heavily doped that the effect of an impurity band is not seen.[4]

II. CALCULATION OF FRACTIONAL CHANGE IN RESISTIVITY AS A FUNCTION OF TEMPERATURE FOR BROOKS-HERRING SCATTERING

In the Thomas-Fermi approximation, the screened Coulomb potential for an electron interacting with a singly ionized donor is

$$V(\mathbf{r})=-e^2e^{-qr}/\kappa r\,, \tag{1}$$

where κ is the static dielectric constant of the semiconductor and q is the Thomas-Fermi inverse screening length. In the Born approximation the transition probability that an electron with wave vector $\mathbf{k}$ is scattered into a state with wave vector $\mathbf{k}'$ is proportional to $[(\mathbf{k}-\mathbf{k}')^2+q^2]^{-2}$. Typically, q and the diameter of the Fermi sphere (which equals the maximum change in wave number due to intravalley scattering) are always small in comparison with the size of a Brillouin zone. Thus for ν valleys, each separated by a wave vector of the order of a reciprocal-lattice vector, intervalley scattering due to screened ionized impurities is very small compared with the intravalley scattering, and it will be neglected here.

Once intervalley scattering is neglected, the distribution function in any valley is obtained from a Boltzmann equation for the isolated valley. In the Born approximation, the transition probability is a function of $\mathbf{k}-\mathbf{k}'$, which, for an isotropic effective mass m^*, is a function of the angle through which the electron is scattered. Consequently, a relaxation time τ exists which is a function of the energy only, and the conductivity tensor may be written[24]

$$\sigma_{ij}=-\frac{e^2}{4\pi^3}\int\tau(\epsilon)v_iv_j\frac{\partial f_0}{\partial\epsilon}d\mathbf{k}\,,$$

where the integral is taken over all $\mathbf{k}$ space and hence over all the valleys. For isotropic valleys, the conductivity tensor becomes a constant σ times the unit tensor. Integrating over the ν constant-energy spheres yields

$$\sigma=\frac{2\nu(2m^*)^{1/2}e^2}{3\pi^3\hbar^3}\int_0^\infty\epsilon^{3/2}\tau(\epsilon)\left(-\frac{\partial f_0}{\partial\epsilon}\right)d\epsilon. \tag{2}$$

The relaxation time may be obtained from

$$\frac{1}{\tau(\epsilon)}=Nv\int_0^\pi(1-\cos\theta)I(\theta)2\pi\sin\theta\,d\theta\,,$$

where N is the total number of scattering centers, which, for uncompensated samples, equals the number of electrons in the conduction band for a d.d.s., and $I(\theta)$ is the differential scattering cross section for scattering from the screened ionized donors. Using the Born approximation and Eq. (1), we obtain the usual expression[22,25]

$$\tau(\epsilon)=(2m^*)^{1/2}\kappa^2\epsilon^{3/2}/\pi Ne^4f(b)\,, \tag{3}$$

where

$$f(b)\equiv\ln(1+b)-b/(1+b) \tag{4}$$

and

$$b\equiv 8m^*\epsilon/\hbar^2q^2. \tag{5}$$

The low-temperature expansion for σ is obtained by noting that, for $T\ll T_D$, we may employ the Sommerfeld expansion for integrals of the form

$$\sigma(T)=\int_0^\infty\sigma(\epsilon,T)\left(-\frac{\partial f_0}{\partial\epsilon}\right)d\epsilon$$
$$=\sigma(\xi,T)+\frac{\pi^2}{6}\frac{d^2\sigma(\epsilon,T)}{d\epsilon^2}\bigg|_\xi(kT)^2+\cdots,$$

where ξ is the Fermi energy at temperature T. Here we have allowed for the possibility that $\sigma(\epsilon,T)$ may have an explicit temperature dependence due to the temperature dependence of q in Eqs. (3)–(5). Thus, through $O(T^2)$, we have

$$\sigma(T)=A\left[\frac{\xi^3}{f(b_F)}+\frac{\pi^2}{6}\left(\xi^2\frac{d^2}{d\epsilon^2}[\epsilon^3/f(b)]\right)_{\xi_0}\left(\frac{T}{T_D}\right)^2\right], \tag{6}$$

where

$$b_F\equiv 8m^*\xi/\hbar^2q^2\,, \tag{7}$$

A is a constant independent of the temperature, and we have used $\xi_0=kT_D$.

For free electrons moving in three dimensions we have

$$\xi=\xi_0[1-\tfrac{1}{12}\pi^2(T/T_D)^2]\,, \tag{8}$$

[23] J. B. Krieger and S. Strauss, Phys. Rev. **169**, 674 (1968).

[24] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London, 1954), p. 196.

[25] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

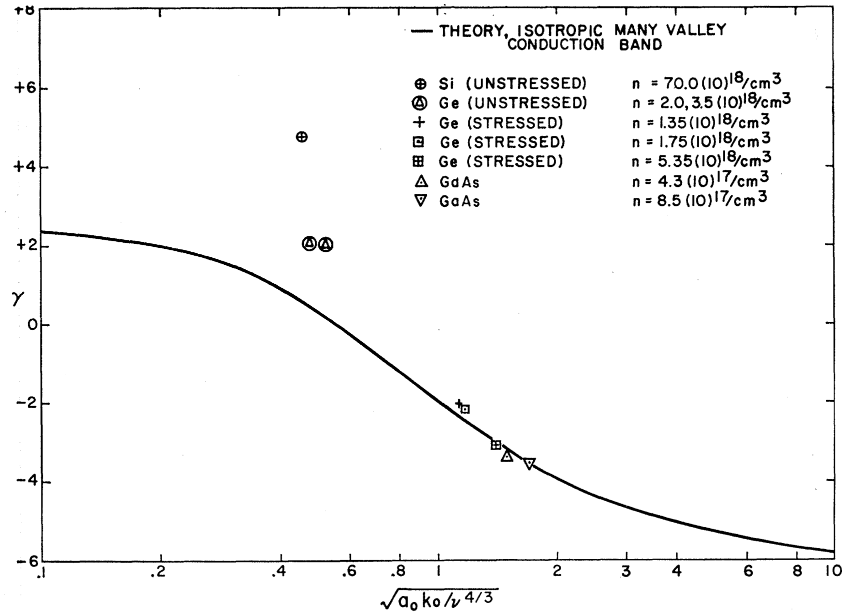

FIG. 2. Coefficient γ versus $(a_0k_0/\nu^{4/3})^{1/2}$, where $\Delta\rho/\rho_0=\gamma(T/T_D)^2$.

and the temperature-dependent Thomas-Fermi inverse screening length is given by[22]

$$q^2=\frac{4\pi e^2}{\kappa}\nu\int_0^\infty g(\epsilon)\left(-\frac{\partial f_0}{\partial\epsilon}\right)d\epsilon,$$

where $g(\epsilon)$ is the density of states for a single valley. Employing the Sommerfeld expansion, using Eq. (8) and the fact that $g\sim\epsilon^{1/2}$ for a parabolic band, we obtain

$$q^2=q_0^2[1-\tfrac{1}{12}\pi^2(T/T_D)^2], \tag{9}$$

with

$$q_0^2/4k_0^2=\nu^{2/3}/\pi a_0k_0, \tag{10}$$

where $k_0=(3\pi^2N)^{1/3}$ is the Fermi wave number at $T=0$ if all the electrons occupied only one valley. Finally, from Eqs. (7), (9), and (10) we find that b_F is independent of T through $O(T^2)$ and is given by

$$b_0=\pi a_0k_0/\nu^{4/3}.$$

Thus the first term in Eq. (6) may be written

$$\frac{A\xi^3}{f(b_F)}=\sigma(0)\left[1-\frac{\pi^2}{4}\left(\frac{T}{T_D}\right)^2\right].$$

The second term in Eq. (6) is easily evaluated once it is noted that b is proportional to ϵ. Collecting terms, we obtain

$$\Delta\rho/\rho_0=-\Delta\sigma/\sigma_0=\gamma(T/T_D)^2,$$

where

$$\gamma=\pi^2\left(-\frac{3}{4}+\frac{5b_0^2+7b_0^3}{6(1+b_0)^3f(b_0)}-\frac{b_0^4}{3(1+b_0)^4f(b_0)}\right),$$

and where γ is a monotonically decreasing function of only the dimensionless parameter $a_0k_0/\nu^{4/3}$. A plot of γ versus $(a_0k_0/\nu^{4/3})^{1/2}$ is given in Fig. 2. We also note that

$$\gamma\rightarrow\tfrac{1}{4}\pi^2 \quad\text{for}\quad a_0k_0/\nu^{4/3}\rightarrow 0$$
$$\gamma\rightarrow-\tfrac{3}{4}\pi^2 \quad\text{for}\quad a_0k_0/\nu^{4/3}\rightarrow\infty.$$

The doping density required for complete degeneracy may be obtained from the condition that the screening is sufficiently strong to make the binding energy of an electron bound to a screened donor equal to zero.[4] If The Thomas-Fermi approximation is assumed for the screened Coulomb potential, this condition is approximately equivalent to[3]

$$a_0k_0/\nu^{4/3}\geq\pi/4\nu^2. \tag{11}$$

Thus for $\nu=1$, we see from Fig. 2 that $\gamma<0$ and the resistivity will decrease as T increases. However, for the many-valley case, e.g., $\nu=4$ for Ge and $\nu=6$ for Si, the contribution to γ from electron-ion scattering can be positive or negative, depending on the doping concentration.

It is easy to see why electron-ion scattering can give a positive temperature coefficient[15] from the following qualitative argument. The transition probability for scattering from $\mathbf{k}$ to $\mathbf{k}'$ is proportional to $[(\mathbf{k}-\mathbf{k}')^2+q^2]^{-2}$; and as the temperature is increased, q decreases, but the average $\mathbf{k}$ and $\mathbf{k}'$ values increase. When q is large compared with the average change in wave number Δk, then the scattering increases as T increases. If, however, q is small compared with Δk, then the reverse occurs. Now if k_F is the Fermi wave number for electrons distributed in ν valleys, then we have $k_F=k_0/\nu^{1/3}$, and Eq. (10) can be written

$$4k_F^2/q_0^2=\pi a_0k_0/\nu^{4/3}.$$

Now, using Eq. (11), we see that it is possible to have

a large range of doping densities such that a many-valley d.d.s. will have $4k_F^2 < q_0^2$ and hence $\Delta k \ll q_0$, with a resultant increase in the scattering as T increases and hence a positive temperature coefficient.

III. COMPARISON WITH EXPERIMENT

The measured values of γ, plotted in Fig. 2, were obtained by evaluating the slopes of the straight lines in Fig. 1. The appropriate value of $a_0k_0/\nu^{4/3}$ was calculated by taking the density-of-states mass $m^* = 0.072m_0$ and $\kappa = 13.5$ for GaAs,[26] $m^* = 0.22m_0$ and $\kappa = 16$ for Ge,[27] while $m^* = 0.33m$ and $\kappa = 11.7$ for Si.[8] Katz's Ge data are for the transverse case. We find for the single-valley cases that not only is the scaling law satisfied in that the higher a_0k_0 materials have a more negative γ, but there is also good quantitative agreement between theory and experiment. We find the latter somewhat surprising, since the isotropic mass approximation for Ge is rather crude because the actual mass ratio for the constant-energy ellipsoid is 19:1. Furthermore, we have neglected corrections from higher-order Born approximation, multiple scattering, and dressing effects,[26] besides corrections to the Thomas-Fermi screening formula[23] required by the Friedel sum rule for the phase shifts.[28] Moore and Ehrenreich found that the inclusion of the former corrections accounted for the discrepancy of nearly a factor of 2 between the experimental and theoretical values of the mobility in GaAs. However, none of the above-mentioned corrections depends upon the particular dopant present, and hence none can account for the observed fact that the resistivity varies with dopant in a given semiconductor.[29] Nevertheless, the good agreement between theory and experiment for the available data for the single-valley case suggests that our result may be quite accurate in general, despite the omissions of the corrections mentioned above. Data over a wider range of doping densities for other host crystals would help clarify the situation.

For the many-valley case, the agreement between the theoretical calculation and experimental results is poor, the theory consistently giving values of γ which are much lower than the measured values. In fact, from Fig. 1 we find that for Si, $\gamma \approx 6.4$ instead of ≈ 1.4 predicted by theory at $a_0k_0/\nu^{4/3} = 0.1$. This result is greater than the largest possible theoretical value by more than a factor of 2, which demonstrates that no choice of effective mass will lead to agreement between theory and experiment in this case. This result indicates a limitation of the isotropic valley model and suggests a contribution from intervalley electron-electron scattering. The latter will make a positive contribution to the resistivity, because the constant-energy surfaces in each valley are ellipsoidal and not spherical for Ge and Si, a previous calculation for Ge having, demonstrated that this effect is of the order of magnitude necessary to explain the experimental results.[17] However, we do find that the contribution to γ from electron-ion scattering does not make an insignificant contribution to the total γ in the many-valley case and must be included in any accurate theory of the low-temperature behavior of the resistivity.

An alternative explanation of the large temperature dependence of the resistivity in degenerate silicon has been proposed by Long *et al.*[8] They find that both the magnitude of the mobility and its temperature dependence can be understood if resonant scattering is assumed, i.e., $\delta_0 \approx \frac{1}{2}\pi$. However, it appears to us that such scattering is impossible for singly ionized impurity scattering, since the Friedel sum rule restricts the zeroth phase shift δ_0 to be smaller than $\frac{1}{2}\pi$. Furthermore, for many-valley semiconductors, δ_0 must be much smaller than $\frac{1}{2}\pi$. The latter follows from the fact that each valley gives a contribution of

$$\frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1)\delta_l$$

electrons to the screening charge, so that for ν valleys

$$\sum_{l=0}^{\infty} (2l+1)\delta_l = \frac{\pi}{2\nu}$$

for singly ionized scattering, and hence $\delta_0 < \pi/2\nu \approx 0.27$ for unstressed silicon.

Finally, we note that the $T^{3/2}$ dependence of $\Delta\rho/\rho_0$ for antimony-doped germanium[19] cannot be understood in terms of a degenerate electron-gas scattering from screened ionized impurities, and it continues to be an anomaly requiring further study.

ACKNOWLEDGMENT

We are grateful to Dr. D. Long of the Honeywell Corporate Research Center for the original data plots of the low-temperature Si and GaAs data.

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[26] F. J. Moore and H. Ehrenreich, Solid State Commun. **4**, 407 (1966); Phys. Rev. **160**, 618 (1967).

[27] E. Paige, in *Progress in Semiconductors*, edited by A. F. Gibson *et al.* (John Wiley & Sons, Inc., New York, 1964), Vol. 8, pp. 141, 145.

[28] J. Friedel, Phil. Mag. **43**, 153 (1952); F. Stern, Phys. Rev. **158**, 697 (1967).

[29] P. Csavinszky, J. Phys. Soc. Japan **16**, 1865 (1961); **23**, 276 (1967).