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Central-cell corrections to the theory of ionized-impurity scattering of electrons in silicon

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The central-cell correction to the impurity potential for ionized-impurity scattering has been examined in detail. This was then included with the Coulomb and phonon scattering as calculated by Ito and Herring and Vogt for the anisotropic conduction-band valley to determine the theoretical mobility. The central-cell correction was calculated in the spherical approximation with a potential determined empirically from the bound-state energies of the donor, with many-valley effects included. It is shown that the main part of the strain scattering is included as a small component in this empirical potential. The scattering is calculated with Green's-function methods and accounts for most of the observed resistivity, although a discrepancy remains. Similar calculations are reported for the case of Ge.

I. INTRODUCTION

Impurity scattering is the dominant process governing electron mobility in semiconductors at low temperatures and remains important at room temperature at moderate levels of doping. A detailed understanding of the impurity scattering from a theoretical standpoint is therefore of great interest, and a complete treatment would be very valuable in allowing the prediction of mobilities for a given level of doping or, conversely, prediction of the doping level from a measurement of the mobility. While there has been a considerable amount of theoretical discussion in the past 25 years, it seems to us that no completely satisfactory theory is yet available. The pioneering work of Brooks and Herring,[1] who assumed a screened Coulomb potential and spherical energy bands, gives a good order-of-magnitude agreement with experiment, but there remains a sizeable discrepancy, as recently pointed out by Rode.[2]

In this paper we examine the effects which arise from the fact that the screened Coulomb form of the interaction breaks down at short distances when the electron is on the impurity atom itself. This leads to a well-known chemical shift in the bound-state energy of the impurity.[3,4] We shall make a more detailed calculation of the effect of this local potential on the scattering than has previously appeared. Other workers, for example, Csavinszky,[5] have suggested that the effect will be small. In Fig. 1 we show a collection of experimental Hall mobilities plotted versus the inverse of the Hall number; the size of the discrepancy between theory and experiment is apparent. Although there is a considerable scatter in the experimental data, the mobilities of P-doped Si do seem to be significantly smaller than those of As- and Sb-doped specimens. This observation suggests that the effects of the local potential are not unimportant.

Recently Daga and Khokle[6] have reported a calculation of the effect of the strain-induced potential surrounding ionized impurities. They appear to conclude that this mechanism can explain the discrepancy, but we believe their calculations to be unsatisfactory in several respects detailed in Sec. VI. Indeed their theory cannot explain the discrepancy for all group-V donors, as the sign of their correction depends on whether the donor ion is larger or smaller than the host. Experimentally the correction has the same sign for all donors. Instead, we find that the main part of the strain effect is already included in the short-range potential, if this is chosen empirically to give the correct bound-state energy.

The many-valley nature of the conduction band in Si and Ge complicates the calculations. We include this in our treatment of the impurity scattering. It also introduces extra scattering from the strains which we can only estimate approximately. The ellipsoidal form of the valleys also complicates the analysis and introduces a correction to the Brooks-Herring term itself.

The paper is mainly concerned with the results in Si, but a short discussion of the effect in Ge is given. We find that our treatment goes a long way towards explaining the observed resistivity, but a discrepancy still remains which must arise from other scattering mechanisms.

II. IMPURITY SCATTERING

The potential due to an ionized impurity varies with position in a way which reflects the atomic structure of the medium. The scattering should be calculated from the Bloch electron states, which also reflect the atomic structure. However, near the band extrema, it is found that the effective-mass approximation[7] is valid, and the effects may be calculated from an effective potential acting be-

tween free-particle states, where the atomic structure is ignored except for the introduction of an effective mass. In this approximation the electron wave function can be expressed, except close to the impurity, as a modulated Bloch function

$$\psi(\vec{r}) = \Omega^{1/2} \sum_i F_i(\vec{r})\, \chi_i(\vec{r}) ,$$

where $\chi_i(\vec{r})$ is the Bloch function at the center of the valley i, and the envelope function $F_i(\vec{r})$ obeys the effective-mass equation. In the effective-mass approximation χ is transformed away and the effective potential due to the impurity which appears in the Schrödinger equation is that of a point charge in a dielectric medium screened by the presence of other electrons. Near the central impurity the irregularity of the atomic potential may be included in the effective potential as an extra short-range interaction represented by a delta-function pseudo-potential. The potential $\mathfrak{U}$ is localized; so we define

$$\mathfrak{U}(\vec{r}, \vec{r}') = U(r)\delta(\vec{r} - \vec{r}')$$

and

$$U(r) = -(e^2/\epsilon r)e^{-r/\lambda} + V\delta(\vec{r}) , \qquad (1)$$

where the screening length λ is given by

$$\lambda^2 = \epsilon k_B T / 4\pi e^2 N_I .$$

Throughout this paper we assume that the electrons have the same density as the ionized impurities (i.e., no compensation) and that the temperature T is high enough for classical statistics to be obeyed. In (1), $U(r)$ has the dimensions of energy, $\mathfrak{U}$ has dimensions of energy/volume, and the dimensions of V are energy$\times$volume.

The scattering properties are conveniently described in terms of Green's functions defined in terms of the envelope function

$$G(\vec{r}, \vec{r}', E) = \sum_n \frac{F_n(\vec{r})\, F_n(\vec{r}')^*}{E - E_n + i\delta} , \qquad (2)$$

where the sum is over all states n. The F are normalized to the crystal volume Ω; so G has the dimensions of (energy$\times$volume)$^{-1}$. The energy E is given a small imaginary part δ. For the perfect crystal with no impurities the Green's function G_0 is obtained using plane-wave states for F. The T matrix which gives the total scattering due to $\mathfrak{U}$ is

$$T(\vec{r}, \vec{r}') = \mathfrak{U}(\vec{r}, \vec{r}') + \int \mathfrak{U}(\vec{r}, \vec{r}'')\, G_0(\vec{r}'', \vec{r}''', E) \times \mathfrak{U}(\vec{r}''', \vec{r}')\, d\vec{r}''\, d\vec{r}''' + \cdots , \qquad (3)$$

which can be written formally as

$$T = (1 - G_0\mathfrak{U})^{-1}\mathfrak{U} . \qquad (4)$$

The rate of scattering from $\vec{k}$ to $\vec{k}'$ is proportional to the square of the Fourier transform of T

$$T(\vec{k}, \vec{k}') = \frac{1}{\Omega} \int T(\vec{r}, \vec{r}')\, e^{-i\vec{k}\cdot\vec{r}}\, e^{i\vec{k}'\cdot\vec{r}'}\, d\vec{r}\, d\vec{r}' . \qquad (5)$$

By the optical theorem the total transmission rate out of $\vec{k}$ is given by

$$-2\,\mathrm{Im}\,T(\vec{k}, \vec{k}) = \hbar/\tau(k) ;$$

however, the mobility is related to the weighted average

$$\frac{\hbar}{\tau(k)} = 2\pi \sum_{\vec{k}'} \left| T(\vec{k}, \vec{k}') \right|^2 (1 - \cos\theta_{\vec{k}\vec{k}'}) \times \delta[E(\vec{k}') - E(\vec{k})] , \qquad (6)$$

where $\theta_{\vec{k}\vec{k}'}$ is the angle between the group velocities $\nabla_k E(\vec{k})$ at $\vec{k}$ and $\vec{k}'$.

In the real many-valley band structure of Si and Ge there are two types of contribution to the sum over $\vec{k}'$, those in the same valley as $\vec{k}$ (intravalley scattering) and those in different valleys (intervalley scattering). In the latter case the randomizing condition of Herring and Vogt is essentially satisfied both for the phonon scattering[8] and, as seen in Sec. V, for the ionized impurity scattering, in which case the average over $\vec{k}'$ leads to a simple density of states $n(E)$ for each valley and (for Si) the relaxation time for intervalley scattering becomes

$$\hbar/\tau_r(k) = 2\pi \left(\left| T_g \right|^2 + 4 \left| T_f \right|^2 \right) n(E) . \qquad (7)$$

The density of states $n(E)$ is related to the imaginary part of G_0 evaluated at $r = r' = 0$,

$$-\pi n(E) = \Omega G_0^I(E) . \qquad (8)$$

The subscript g indicates scattering between opposite valleys, while f represents the four valleys on different axes from that of $\vec{k}$. Since T_f and T_g are independent of $\vec{k}$, $\vec{k}'$, they can be represented by effective short-range potentials V_f and V_g. These will be determined empirically from the valley-orbit splittings of the bound states.

The intravalley scattering is complicated by the anisotropic energy surfaces of the valley, and it is only possible to perform the sum in (6) with an explicit form for $T(k, k')$. In fact this will be done in Sec. III by using the Born approximation for Coulomb scattering when $T(\vec{k}, \vec{k}') \rightarrow \mathfrak{U}(\vec{k}, \vec{k}')$. The relaxation time is now anisotropic, and the electron mobility represents a weighted average over the six valleys,[8]

$$\mu = (e/3\langle E\rangle)\left(\langle E\tau_{\parallel}\rangle/m_{\parallel} + 2\langle E\tau_{\perp}\rangle/m_{\perp}\right) , \qquad (9a)$$

and, for the Hall mobility,

$$\mu_H = e\left(\frac{2\langle E\tau_{\parallel}\tau_{\perp}\rangle}{m_{\parallel} m_{\perp}} + \frac{\langle E\tau_{\perp}^2\rangle}{m_{\perp}^2}\right) \Big/ \left(\frac{\langle E\tau_{\parallel}\rangle}{m_{\parallel}} + \frac{2\langle E\tau_{\perp}\rangle}{m_{\perp}}\right) . \qquad (9b)$$

The angular brackets represent a thermal average over a Maxwell-Boltzmann distribution.

In this paper we shall be particularly concerned with the effect of the central-cell correction on the mobility. This is difficult to estimate in the aniso-

tropic band structure, and we therefore consider an approximation where the band is regarded as spherical for this purpose. Following Long,[9] we are able to treat the anisotropy of the phonon scattering. Consequently, we may sum the individual contributions to the mobility (9) in terms of the relaxation times for phonon scattering, τ_p, Coulomb impurity scattering, τ_i, and the correction due to the central cell, τ_c,

$$(m/\tau)_\alpha = m_\alpha/\tau_p^\alpha + m_\alpha/\tau_i^\alpha + m^*/\tau_c \ . \qquad (10)$$

We estimate m^* by finding the spherical effective mass which gives the closest agreement to the anisotropic Coulomb scattering. We have found that $m^* = 0.30\, m_0$ gives a mobility which differs from the anisotropic result by less than 5% over a wide range; we consequently use this value in (10).

When we do have spherical symmetry we may separate the scattering into partial waves of angular momentum l and

$$T(\vec{k}, \vec{k}') = \frac{1}{4\pi} \sum_l (2l+1)\, T_l(E)\, P_l(\cos\theta_{kk'}) \ , \qquad (11)$$

since the scattering is elastic and $|\vec{k}| = |\vec{k}'| = k$. Then $T_l(E)$ is related to the phase shift $\delta_l(E)$ by

$$T_l = [4\pi/\Omega G_0^I(E)] \sin\delta_l\, e^{i\delta_l} \ , \qquad (12)$$

where $G_0^I(E)$ is given by (8). In this situation the relaxation time for resistivity is[10]

$$\frac{\hbar}{\tau} = -\frac{\Omega G_0^I(E)}{(4\pi)^2} \sum_{l, l'} \int d\theta \sin\theta (1-\cos\theta)\, T_l\, T_{l'}^* \times P_l(\cos\theta)\, P_{l'}(\cos\theta)\, (2l+1)\, (2l'+1) \qquad (13a)$$

$$= -\frac{2\Omega G_0^I(E)}{(4\pi)^2} \sum_l (l+1) \left| T_l - T_{l+1} \right|^2 \qquad (13b)$$

$$= \frac{-2}{\Omega G_0^I(E)} \sum_l (l+1) \sin^2(\delta_l - \delta_{l+1}) \ . \qquad (13c)$$

III. SCREENED COULOMB SCATTERING

The validity of the basic assumptions of Brooks and Herring that the effective impurity potential is given by the screened Coulomb form with the Debye-Huckel screening length has been questioned by Redfield and Afromowitz.[11] They pointed out that for high densities ($N_I > 10^{17}\ \text{cm}^{-3}$ in Si at 300 K) the thermal electron wavelength is longer than the screening length and that the usual assumptions are inadequate in this situation. This is, in our view, somewhat pessimistic since the electron kinetic energy increases and its effective wavelength decreases when it is close to the impurity. Moreover, detailed calculations by Glasko and Mironov[12] obtain a potential which differs little from the classical result up to densities which in Si at 300 K are well in excess of $10^{18}\ \text{cm}^{-3}$. Colbow and Dunn[13] also find that the classical result effectively holds well beyond the density given by the simple criterion. We shall therefore continue to use the Brooks-Herring form as a basis of our estimate to the central-cell effects. It is likely that any serious error is confined to the very high density end of the experimental range.

The screened Coulomb scattering is calculated using the Born approximation. This too is inadequate in the high-density limit, where a full phase-shift analysis is necessary.[14] We have calculated the relaxation times following the method of Ito,[15] who has used the spherical harmonic expansion developed by Herring and Vogt[8] for phonon scattering. Consequently, we have evaluated Ito's Eqs. (25) and (26) for $\tau_\parallel$ and $\tau_\perp$, using the masses $m_\parallel = 0.90$ and $m_\perp = 0.192$. The anisotropy of τ is energy dependent, reaching a maximum value of $\tau_\parallel/\tau_\perp \simeq 4$.

In order to include the central-cell correction we need an effective spherical band. For such a band, in Born approximation,

$$\frac{\hbar}{\tau} = N_I \frac{2\pi e^4 \hbar}{\epsilon^2 m^{*1/2} (2E)^{3/2}} \left(\ln(1+\xi) - \frac{\xi}{1+\xi} \right) , \qquad (14)$$

where $\xi = 4k^2\lambda^2 > 1$. It is convenient to scale all quantities in the natural units of the unscreened Coulomb problem so that lengths are given in Bohr radii and energies in rydbergs. Then

$$k = (\alpha a_0)^{-1} \ \text{and} \ E = R/\alpha^2 \ ,$$

where

$$a_0 = \hbar^2\epsilon/m^* e^2 \ \text{and} \ R = e^2/2\epsilon a_0 \ .$$

The only uncertain parameter is the effective mass m^* of the equivalent isotropic band, which is taken to give agreement with the variationally calculated[3] Coulomb binding energy in the anisotropic case. Ning and Sah[4] have found this to be $m^* = 0.30\, m_0$ in Si.

The phase shifts for the screened Coulomb potential are complicated.[14] When the central-cell potential is included, it will affect δ_0 only since it is a delta function. From (13), it is clear that this only enters the mobility through $\delta_1 - \delta_0$, and we accordingly need this quantity. In the Born approximation

$$\delta_1 - \delta_0 = -\alpha [(1/\xi)\ln(1+\xi) - 1] \ ; \qquad (15)$$

in the region of interest this is approximately equal to α and to the exact result for the unscreened Coulomb case $\delta_1 - \delta_0 = \cot^{-1}(1/\alpha)$.

IV. CENTRAL-CELL CORRECTION

It is convenient to consider the effect of the central cell as a correction, assuming that the effect of the screened Coulomb potential is already known, and taking a spherical band for this purpose. The total T matrix, which includes the Coulomb part

T_C and a correction S, is a solution of the equation

$$G = G_0 + G_0 (T_C + S) G_0 . \quad (16)$$

The Coulomb part is given by

$$G_C = G_0 + G_0 T_C G_0 , \quad (17)$$

and the correction can be written

$$G = G_C + G_C T' G_C , \quad (18)$$

where

$$G_C T' G_C = G_0 S G_0 . \quad (19)$$

Since V is finite only at the origin, only the s wave has a contribution

$$T'(\vec{r}, \vec{r}') = \{V/[1 - V G_C(E)]\} \delta(\vec{r}) \delta(\vec{r}') , \quad (20)$$

where the first factor is a scalar. $G_C(E)$ is $G_C(r, r', E)$ evaluated at $\vec{r} = \vec{r}' = 0$. Thus the extra scattering introduced by V can be directly calculated if G_C is known. The result can be conveniently expressed in terms of phase shifts. If the total s-wave phase shift due to $T_C + S$ is $\delta_0 + \delta_0'$, then it is straightforward to show, using (12), that

$$S(\vec{k}, \vec{k}') = [1/\Omega G_0^I(E)] e^{2i\delta_0} \sin\delta_0' e^{i\delta_0'} . \quad (21)$$

The wave function of the s-wave state of energy E $\psi(r)$ differs from the free-particle wave function at large r by only the phase shift $e^{i\delta_0}$. It can be shown that

$$\lim_{r \to \infty} G_C(0, \vec{r}, E) = \Omega^{1/2} \psi(0)\, G_0(0, \vec{r}, E) e^{i\delta_0} , \quad (22)$$

since states of energy E dominate the Green's function at E. Hence from (19) we find

$$S(\vec{k}, \vec{k}') = \Omega |\psi(0)|^2 T' e^{2i\delta_0} , \quad (23a)$$

or

$$T'(\vec{k}, \vec{k}') = [1/\Omega G_C^I(E)] \sin\delta_0' e^{i\delta_0'} , \quad (23b)$$

as might be expected from (18).

The appearance of G_C, rather than G_0, in the expression for T' gives an enhancement of the scattering which arises from the build up of the electron wave function on the impurity site due to the screened Coulomb potential. The value of V can be determined from the chemical shift of the ground state of an isolated impurity. In this situation the Coulomb interaction is not screened and the energy is given by the pole of T' as, using (20),

$$V^{-1} = G_u(E) , \quad (24)$$

where G_u is the Green's function for the unscreened Coulomb potential. By explicit evaluation of (2) and setting $E = -1/\nu^2$,

$$G_u(E) = (1/2\pi)[\psi(1+\nu) + \pi \cot(\pi\nu) - \ln\nu - 1/2\nu + \gamma - 1/\pi b + \ln b] + O(b) , \quad (25)$$

where ψ is the digamma function, γ is Euler's constant, and $1/b^2$ is the energy bandwidth (in atomic units and hence $b \ll 1$).

The extra scattering is related to δ_0' defined by (23b), which is given by, using (20),

$$\tan\delta_0' = G_C^I(E)/[V^{-1} - G_C^R(E)] . \quad (26)$$

Unfortunately it is difficult to obtain G_C for the screened Coulomb case. A good estimate of δ_0' can, however, be made by using G_u instead. This tends to over estimate the effect since it increases the density at the impurity site by too large a factor. Using Coulomb wave functions in (2) gives, for the energy $E = 1/\alpha^2$,

$$G_u^R(E) = \frac{1}{2\pi}\left(\mathrm{Re}\,\psi(1 + i\alpha) - \ln\alpha + \gamma + \ln b - \frac{1}{\pi b}\right) + O(b) , \quad (27a)$$

$$G_u^I(E) = G_0^I(E)\Omega |\psi(0)|^2 = -\frac{1}{2}\frac{1}{1 - e^{-2\pi\alpha}} . \quad (27b)$$

In this approximation (26) shows that δ_0' is independent of the bandwidth.

An underestimate of δ_0' can be obtained by substituting G_0 into (26) instead of G_C, where

$$G_0^I(E) = -1/4\pi\alpha , \quad (28a)$$

$$G_0^R(E) = -\frac{1}{2\pi^2 b} - \frac{1}{4\pi^2\alpha} \ln\frac{\alpha - b}{\alpha + b} . \quad (28b)$$

Taking $b = 0.1$, corresponding to a bandwidth of 4 eV, we find that the two estimates of δ_0' differ by about 20%. Because of uncertainties in the appropriate value of b we shall work with the pure Coulomb form, anticipating a small overestimate of the effect.

The resultant expression for $\tan\delta_0'$ from (26) and (27) has also been obtained by direct solution of Schrödinger's equation for a Coulomb potential with a central square well in the limit that the width of the well goes to zero. This alternative method, which is summarized in the Appendix, has also been used to demonstrate the insensitivity of the result to the details of the central well.

V. MANY-VALLEY EFFECTS

The calculations of Sec. IV proceeded on the basis of a single spherical band, but, as pointed out in Sec. II, we must also consider intervalley scattering. The local potential V is then a 6×6 matrix for Si with elements $V_{ij} = V_s$ $(i = j)$, V_g (i opposite to j), and V_f (i sideways from j). We assume that the screened Coulomb interaction acts as an intravalley effect only. Its contribution to intervalley scattering is included in the effective potentials V_{ij}. Since $\vec{k}_i - \vec{k}_j$ is nearly constant in intervalley scattering the range of the effective V_{ij} is not significant and can be taken as a delta function.

In this approximation T' and S become 6×6 matrices with the same symmetry as V, i.e.,

$$T'_{ij} = (1 - VG_C)^{-1}_{ik} V_{kj} , \quad (29)$$

where G_C is a diagonal unit matrix in the 6×6 notation with element $G_C(E)$. All these matrices can be diagonalized by the same symmetry transformation to give a singlet A, a doublet E, and a triplet T representation of the cubic group. Then

$$V_s = \tfrac{1}{6}(V_A + 2V_E + 3V_T) ,$$
$$V_f = \tfrac{1}{6}(V_A - V_E) , \quad (30)$$
$$V_g = \tfrac{1}{6}(V_A + 2V_E - 3V_T) ,$$

with similar relations holding for S and T'. The impurity potentials can be obtained by using (24) together with the experimental values of the ground-state energy of each symmetry type. These have been collected by Ning and Sah[4] for Si and are given in Table I. The phase shifts δ_i are then obtained from (24) and (26) using (25) and (27) in each case.

From (13b) we have for the correction to the intravalley relaxation time

$$\frac{\hbar}{\tau_s} = -\frac{2\Omega G_0^I(E)}{(4\pi)^2} \left(|T_0^C - T_1^C + S_s|^2 - |T_0^C - T_1^C|^2 \right) , \quad (31)$$

where the superscript C denotes the Coulomb T matrix and S_s is the symmetrical combination analogous to that in (30).

$$S_s = \tfrac{1}{6}(S_A + 2S_E + 3S_T)$$
$$= \frac{4\pi e^{2i\delta_0}}{\Omega G_0^I(E)} \frac{1}{6} (\sin\delta_A e^{i\delta_A} + 2\sin\delta_E e^{i\delta_E} + 3\sin\delta_T e^{i\delta_T}) \quad (32)$$

The intervalley scattering is given by (7) with S_f and S_g for T_f and T_g,

$$\frac{\hbar}{\tau_r} = -\frac{2\Omega G_0^I(E)}{(4\pi)^2} \left[|\tfrac{1}{6}(S_A + 2S_E - 3S_T)|^2 + 4|\tfrac{1}{6}(S_A - S_E)|^2 \right] , \quad (33)$$

and is added to (31) to give the total correction (10). Here S is the $l=0$ expansion coefficient of $S(\vec{k}, \vec{k}')$ equivalent to Eq. (11).

VI. STRAIN SCATTERING

If silicon is assumed to be elastically isotropic the displacements $\vec{u}(\vec{r})$ of an atom at point $\vec{r}$, far from the impurity at the origin, can be expressed[16] as

$$\vec{u}(\vec{r}) = (\Delta\Omega/4\pi)\, \vec{r}/r^3 , \quad (34)$$

where $\Delta\Omega$ is the extra atomic volume occupied by the donor impurity. The effective potential arising from such a strain is

$$V(\vec{r}) = \Xi_d \nabla\cdot \vec{u}(\vec{r}) - 2\Xi_u P_2(\cos\theta)/r^3 , \quad (35)$$

where Ξ_d and Ξ_u are the deformation potentials and θ is the angle between $\vec{r}$ and the major axis of the effective mass tensor. It is difficult to solve the scattering problem with an anisotropic potential without making some severe approximations. A good idea of the effect of the strain can be obtained, however, by assuming the existence of a single valley at the middle of the Brillouin zone and assuming the deformation-potential approximation to hold even close to the impurity. In this case the effective potential becomes

$$V(\vec{r}) = E_1 \nabla\cdot \vec{u}(\vec{r}) = E_1 \Delta\Omega\delta(\vec{r}) , \quad (36)$$

where E_1 is the appropriate deformation potential.[17] It gives a contribution to the delta-function potential we have already considered. Since V was chosen to fit the observed bound-state energies the effect has already been included in the empirical determination of V.

This contribution to V can be estimated using a value for E_1 determined by fitting the acoustic phonon mobility in the same isotropic model. E_1 was adjusted to fit the Hall mobility in the isotropic model with a mass of $0.3\, m_0$ to the Hall mobility obtained from Long's model[9] using his parameters. The oversize of the impurity can be estimated to be about 2.5 Å^3 for the case of phosphorus from the x-ray data of Cohen.[18] There is some scatter in the literature, but this figure is consistent with the data of Pearson and Bardeen.[17] Daga and Khokle[6] give a summary of the available evidence on other donors which have size mismatches of a similar magnitude. The result gives a contribution to V of about 0.03 a.u., while values estimated from (24) are much larger. For example, using the 45 meV binding energy of phosphorus, and assuming a band width of 3 eV, a value of 0.65 a.u. for V is obtained from (24). A calculation outlined in the Appendix gives correction for the mobilities of less than 1% compared with central-cell corrections of the order of 10% when a square well of radius 1 Å was used.

As well as the anisotropic form in the effective potential due to the strain, effects arise from the elastic anisotropy and the effective-mass anisotropy. Nevertheless, the magnitude of the effects due to anisotropy can reasonably be expected to be no larger than that of the isotropic part just considered, which was seen to be small.

The recent results of Daga and Khokle[6] show a much larger correction than calculated here. They

TABLE I. Energy levels of donors in silicon.

	E_A (meV)	E_E (meV)	E_T (meV)
P	45.5	32.4	33.7
As	53.7	31.2	32.6
Sb	42.7	30.4	32.8
Bi	72.9		32.2
Coulomb	30.9	30.9	30.9

have, however, made a number of assumptions which do not appear to be justified. For example, they assume that the strain field causes no displacements beyond the first neighbors and that the perturbing potential arises from charges on these neighbors screened in the Debye-Huckel manner. The change in potential due to the symmetric displacements of these atoms in the strain field is that of a screened octopole at large distances, but they appear to use a screened Coulomb form. There is also difficulty in determining what their final result is because they find a temperature-dependent reduction of mobility in their first paper but quote a temperature-independent one in the second. We conclude therefore, in disagreement with Daga and Khokle,[6] that the strain effect is not particularly important—in any case it is largely included in the phenomenological value of V.

VII. RESULTS

A. Silicon

The Hall mobility due to anisotropic Coulomb scattering has been calculated using the methods described in Sec. III and Eq. (9b). The phonon scattering processes for pure silicon have been added to the scattering rates to produce a mobility which may be compared with experiment.

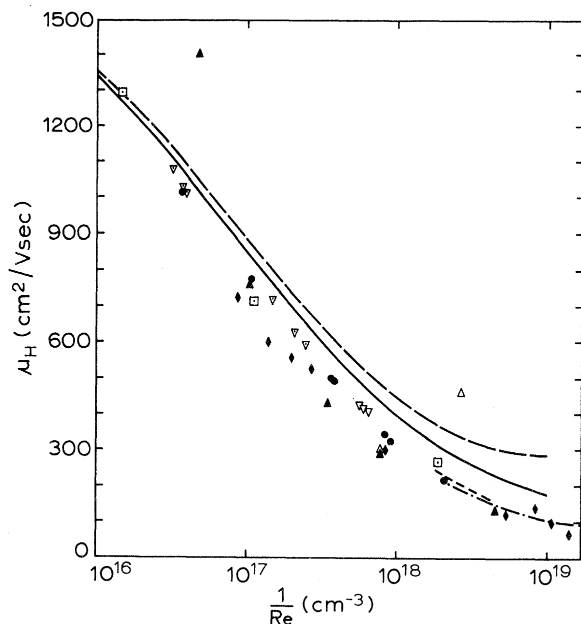

FIG. 1. Hall mobility at 300 K vs the reciprocal of the Hall coefficient for uncompensated silicon. Upper curve represents the combined effects of phonon and Coulomb scattering in anisotropic bands. Lower curve included the central-cell scattering calculated for phosphorus. Experiments are represented by points which differentiate authors and donor species: ⊡ (As) Morin and Maita (Ref. 19); ▲ (P), Δ (Sb), ◬ (As) Brinson and Dunstan (Ref. 20); ⧫ (P) Gränacher and Czaja (Ref. 21); ▽ (Sb), ▿ (As) Wolfstirn (Ref. 22); • (P) Goldsmith and Berz (Ref. 23); dashed line (Sb), dot-dash line (As) Furukawa (Ref. 24).

In Fig. 1 we show a collection of experimental data[19–24] of Hall mobility μ_H plotted against $(Re)^{-1}$, where R is the Hall number. This figure is similar to that shown by Rode,[2] but we have been careful to plot only the Hall mobilities. Apparently, corrected mobilities have sometimes been used by Rode. Also shown in the figure is the calculated curve due to phonon and anisotropic Coulomb scattering. The agreement is good at low densities where the impurity scattering is unimportant, but gets progressively worse as the impurity density rises. The theoretical mobility is too large by a factor of about 2 at a density of about $10^{19}/\text{cm}^3$.

The central-cell correction has been added to the impurity scattering in the way described by Eq. (10) and using the results (31)–(33). Each of the phase shifts was obtained from Eq. (26) using expressions for G_u in place of G_C, Eqs. (24), (25), and (27), the value of ν being obtained from the corresponding value of the binding energy listed in Table I. In Fig. 2 we demonstrate the size of the correction by showing the drift mobility limited only by impurity scattering as a function of temperature at a fixed impurity density of $10^{18}/\text{cm}^3$. The result for each of the four Group V donors is shown, and we see a clear chemical shift; in particular, Sb limits the mobility less than the other donors. The energy of the $1s(E)$ level of bismuth has not been measured, but it can be guessed to be somewhere between the hydrogenic value and the value for the $1s(T_2)$ level. The curve in Fig. 2 was evaluated using the latter limit. It is seen from Fig. 2 that, although the central-cell correction to the binding energy to bismuth is larger than to the other donors, its effect on the scattering is not particularly different from the phosphorus or arsenic cases. This anomalous behavior is brought about by the relative complex phases of $T_0 - T_1$ and S in Eq. (31) which are not linear in the central-cell potential. At very low energies it is even possible for the central-cell potential to decrease the scattering strength.

The total mobility (including phonon scattering) for P-doped silicon is also shown in Fig. 1. There is a small chemical shift between donors which is not shown; for instance, at a density of $10^{19}/\text{cm}^3$ Sb gives a mobility of 205 cm^2/V sec in contrast to 175 for P. We see a distinct improvement in the agreement with experiment, most noticeably in the high-density region. However, it is clear that all the resistance has not been accounted for and other scattering mechanisms should be considered. For instance, it has been shown by several authors[25–27] that electron-electron scattering modifies the ef-

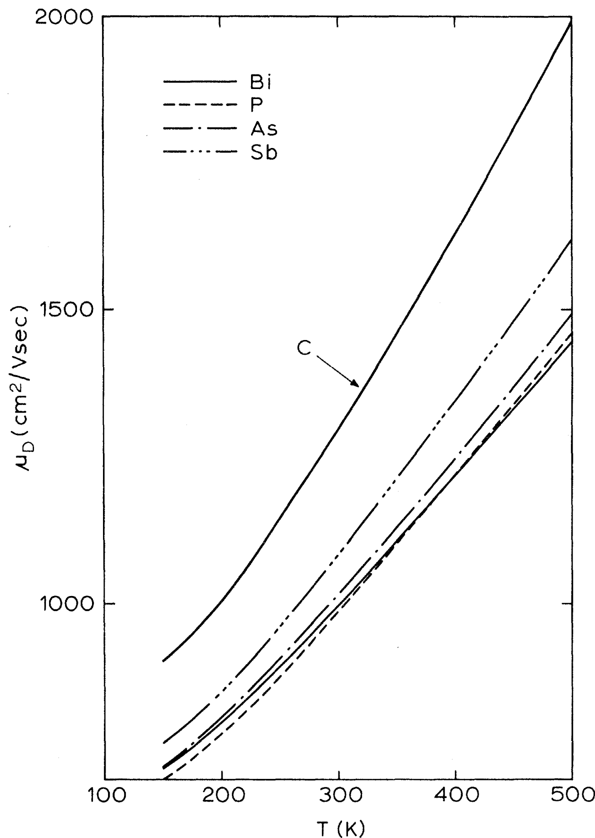

FIG. 2. Calculated drift mobility in silicon vs temperature for an impurity density of $10^{18}/cm^3$. Upper full line refers to a Coulomb potential, the other curves to each donor species.

fect of other scattering processes by redistributing the momenta of the electrons. In the extreme case of Coulomb scattering from impurities being dominant the mobility is reduced by a factor of about 40%. Whilst it is not expected to have such a large effect in our case, it would certainly serve to reduce the residual difference between theory and experiment. Moreover, as pointed out in Sec. III, the screened Coulomb potential is itself suspect at higher densities. Clustering of defects may also produce a modification in this region. There is no shortage of candidates to explain the discrepancy, and we have not been able to estimate their relative effects.

B. Germanium

We will now briefly discuss the effects of the central-cell correction in Ge. Because of the very large anisotropy of the bands in Ge, we have less confidence in our approximations than for Si, and consequently we have not tried to compare theory and experiment directly. The donor energy levels

TABLE II. Energy levels of donors in germanium.

	E_A (meV)	E_T (meV)
P	12.9	10.1
As	14.2	9.9
Sb	10.3	10.0
Bi	12.8	9.9
Coulomb	9.8	9.8

in Ge have recently been listed by Hale[28] and are given in Table II.

In Ge there are four conduction-band valleys, and the valley-orbit splitting gives rise to a singlet and a triplet energy level of the impurity. Although the hydrogenic Bohr radius in Ge is more than double than that of Si,[3] there is still a sizeable central-cell correction to the donor energy levels.

The central-cell correction to the electron mobility has been calculated in a way similar to that of Si by using an effective mass of 0.17—that mass which gives the correct Coulomb binding energy. The results are shown in Fig. 3 for the impurity-scattering limited mobility versus temperature at a density of $10^{18}/cm^3$. The correction is seen to be large, and again Sb limits the mobility less than

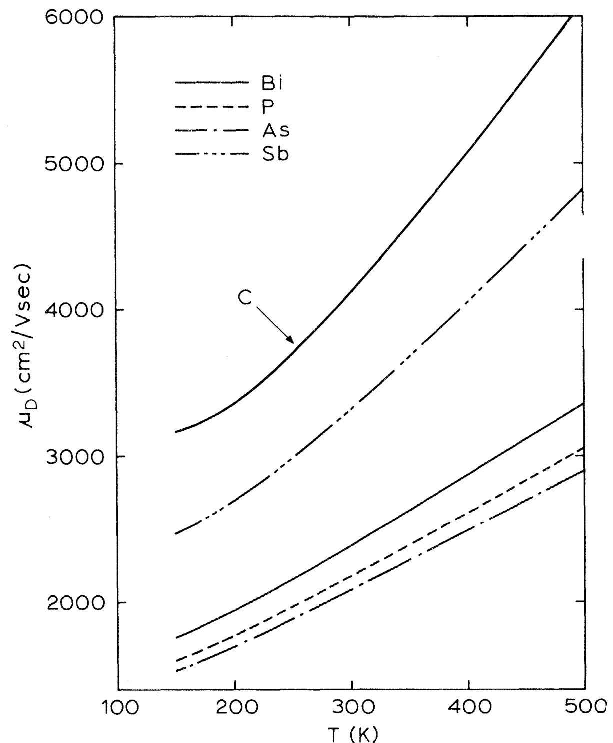

FIG. 3. Calculated drift mobility in germanium vs temperature for an impurity density of $10^{18}/cm^3$. Upper full line refers to a Coulomb potential, the other curves to each donor species.

the other donors. Because of the spherical mass approximation we cannot be certain of the magnitude of the correction; we do notice, however, that both Furukawa[29] and Cuttriss[30] have shown clear chemical shifts in the mobility between Sb and As donors, Sb giving the larger mobility.

VIII. CONCLUSIONS

Coulomb scattering, even when the anisotropy of the conduction-band valleys is taken account of, is insufficient to describe the electron mobility in n-type silicon. By making use of the known deviations from the Coulombic energy levels of the donors and the valley-orbit splitting, we have calculated the mobility of electrons scattering from the different Group-V impurities. The correction is large at high impurity densities but is not sufficient to obtain agreement with the experiments; it is clear that other scattering mechanisms also play a role, and we have indicated some other important corrections. Finally we have estimated the correction to Coulomb scattering in Ge and found it also to be large and to be significantly different for different impurities.

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APPENDIX

A. Schrödinger-equation derivation of δ_0'

In Sec. IV, expression (26) was derived from $\tan\delta_0'$ for Coulomb scattering using the properties of the Coulomb Green's functions. The same expression can be derived from the solutions to Schrödinger's equation. In this case the infinite bandwidth forces the use of a central potential well of a finite radius:

$$U(r) = -e^2/\epsilon r \qquad r > r_0$$
$$= -V_0\,, \qquad r < r_0\,. \tag{A1}$$

The radius of the central-cell correction to the potential is much less than the natural unit of length; so the solutions to Schrödinger's equation for the two regions of space can be conveniently expanded about the origin for the purpose of matching at r_0. Again, for a given small radius r_0, a value for $\tan\delta_0'$ can be found in terms of V_0, which can in turn be expressed in terms of ΔE_0 (or of ν). Taking the limit of small r_0 reproduces (26).

It is of considerable interest to see how the values obtained for $\tan\delta_0'$ vary with r_0. This not only shows how well the small-radius limit can represent more realistic radii but also gives some idea how important the exact form used for the central potential is. Figure 4 shows $\tan\delta_0'$ plotted against the depression of the ground state ΔE_0 for $r_0 = 0.05$ and zero. Not much difference exists between the two curves.

In calculations of the ground-state energies it is sometimes assumed that it is sufficient to use a variational calculation to fix the wave function in the presence of a central well.[4,28] In the present case we find that a variational or a first-order perturbation calculation is insufficiently accurate for the magnitude of the central-cell potential involved. Using first-order perturbation theory gives, in terms of the increased ground-state binding energy,

$$\tan\delta_0' = \tfrac{1}{2}\pi(1 - e^{-2\pi\alpha})^{-1}\Delta E_0/R\,, \tag{A2}$$

by putting V for T' in (23a) and using the first-order expression for ΔE $(= V/\pi a_0^3)$. This expression for $\tan\delta_0'$ is also displayed in Fig. 4. It is not easy to make a variational calculation from the scattering case, but it is possible, for example, to use a variational calculation for binding energy and the first-order expression obtained from (23a). This has been done using $e^{-r/\alpha}$ for the trial function and a central square well with a radius of $r_0 = 0.05$.

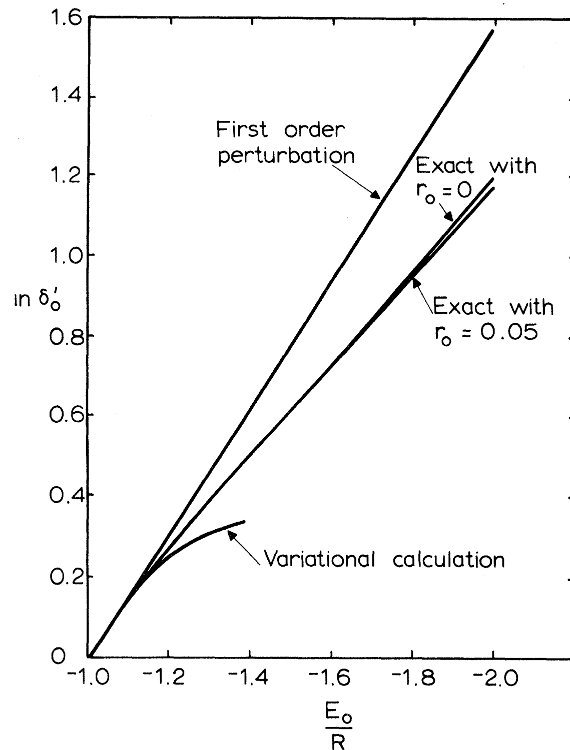

FIG. 4. Variation of s-wave phase shift with ground-state binding energy of the Coulomb potential in the presence of a central spherical square-well potential. Variational calculation was done using a $r_0 = 0.05$ and the perturbation calculation with $r_0 = 0$.

The resulting expression for $\tan\delta_0'$ is also displayed in Fig. 4. It can be seen that neither of these calculations give satisfactory values for $\tan\delta_0'$ for any value of ΔE_0 greater than about 0.1.

B. Estimation of strain effect

The importance of the strain scattering was investigated using the Schrödinger-equation method. The potential used was taken to be the same for intervalley and intravalley scattering. The total strength (integration over all space) of the potential is given by Eq. (36). For a given strength the phase shift δ_0 increases rapidly as the radius r_0 is made smaller; so it is necessary to use a reasonable choice of r_0 in order to get a meaningful result. The value of r_0 chosen was 0.05, which corresponds to a 1 Å in silicon. A somewhat larger figure is probably more realistic; so the small effect found is probably in reality even smaller.

Note added in proof. Price and Hartman [J. Phys. Chem. Solids 25, 567 (1974)] have calculated the intervalley scattering rate due to As in Ge obtaining a result nearly twice what we obtain. Most of this difference can be attributed to their use of first-order perturbation theory.

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