PHYSICAL REVIEW VOLUME 185, NUMBER 3 15 SEPTEMBER 1969

Asymptotic Form of Charge Screening in an Electron Gas of Arbitrary Degeneracy*

L. C. R. Alfred and D. O. Van Ostenburg
Argonne National Laboratory, Argonne, Illinois 60439
(Received 7 March 1969)

Expressions for the long-range screening field around a localized point charge in an electron gas of arbitrary degeneracy have been obtained by evaluating the Dirac density integral for a scattered plane wave and appropriate expansions of the Fermi-Dirac function. The results present a more comprehensive account of the variation of long-range screening with distance and electron-gas degeneracy than has yet been given. It is found that corrections to simple standard forms like the Friedel oscillations and the Brooks-Herring screened Coulomb are quite complex and more significant than generally believed. In the alkali and noble metals these corrections can reverse the sign, and change by a sizable factor the magnitude, of the interaction given by the Friedel expression at the first-neighbor distance.

I. INTRODUCTION

The long-range screening field around a localized point charge in a Fermi-Dirac electron gas is of interest in several areas of the physics of materials. It plays a particularly central role in the study of hyperfine interaction in metallic alloys and doped semiconductors,[1] and in problems on the structure of liquid metals.[2] In practice, it is usually assumed that this long-range screening can be approximated by the Friedel wiggle[3] ($\sim r^{-3}$) in a gas of low degeneracy, and by the Brooks-Herring screened Coulomb[4] in a nondegenerate gas. These simple analytical functions, however, should be used with caution, because they are only limiting forms of complex mathematical expressions and are strictly valid over some particular range of distance and temperature. Serious errors could result if they are employed outside that restricted range without the appropriate corrections or without ascertaining if these corrections are really negligible. It is only recently that efforts have been made to improve on these approximate screening fields. Kohn and Vosko,[5] Flynn and Odle,[6] and Adawi[7] have discussed some temperature corrections to the Friedel wiggle in a gas of low degeneracy. Alfred and Van Ostenburg,[8] on the other hand, following Friedel,[3] have considered higher-order distance corrections to the Friedel expression for the case of complete degeneracy. In the case of a nondegenerate gas, Kochelaev[9] and Adawi[7] have indicated that the long-range screening has a Gaussian rather than an inverse exponential factor. Several numerical solutions of the problem have also been reported by Langer and Vosko,[10] and by March and Murray.[11,12] These previous investigations, however, particularly those yielding analytical results, have been fragmentary. They certainly demonstrated that important corrections were being overlooked, but the essential results are not general or detailed enough to permit a reasonably accurate treatment of most charge screening problems within the free-electron framework.

In the present investigation, an attempt is made to account more comprehensively than has yet been done for the variation with both distance and degree of degeneracy of the tail of the charge screening field in a noninteracting Fermi-Dirac electron gas. The results are derived from first principles in a quasi-Hartree self-consistent scheme by evaluating the Dirac density integral[11] for a scattered plane wave and appropriate expansions of the Fermi-Dirac function. The expression for the screening field are given in their most general form for the degeneracies of interest. The main features of the results are discussed and compared with previous work.

II. THEORY OF LONG-RANGE CHARGE SCREENING IN AN ELECTRON GAS

A. Density of Screening Charge Cloud

The density of the screening charge cloud $\delta\rho(r)$ around a localized point charge in a noninteracting Fermi-Dirac electron gas is given by

$$\delta\rho(r)=\frac{1}{4\pi^3}\int d\mathbf{k}(\psi\psi^*-1)F(k)\,, \tag{1}$$

where ψ is the perturbed wave function of the charge carrier, $F(k)$ is the Fermi-Dirac distribution function

* Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] R. E. Watson, *Hyperfine Interactions* (Academic Press Inc., New York, 1967), p. 413; N. J. Horing, J. Phys. Soc. Japan Suppl. **21**, 704 (1966).

[2] J. E. Enderby and N. H. March, Advan. Phys. **16**, 691 (1967).

[3] J. Friedel, Nuovo Cimento Suppl. **2**, 287 (1958).

[4] P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).

[5] W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).

[6] C. P. Flynn and R. L. Odle, Proc. Phys. Soc. (London) **81**, 412 (1963).

[7] I. Adawi, Phys. Rev. **146**, 379 (1966).

[8] L. C. R. Alfred and D. O. Van Ostenburg, Phys. Letters **26A**, 27 (1967).

[9] I. Kochelaev, Fiz. Tverd. Tela **7**, 2859 (1965) [English transl.: Soviet Phys.—Solid State **7**, 2315 (1966)].

[10] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids **12**, 196 (1959).

[11] N. H. March and A. M. Murray, Proc. Roy. Soc. (London) **A261**, 119 (1961).

[12] N. H. March and A. M. Murray, Proc. Phys. Soc. (London) **79**, 1001 (1962).

$1+\exp[\hbar^2(2m^*k_BT)^{-1}(k^2-k_T{}^2)]$, with k_B denoting the Boltzmann constant; T is the absolute temperature, m^* is the effective mass of the carrier, k is a wave number, and k_T is the Fermi-Dirac normalization constant at temperature T. In the region where the effective potential of the localized charge is negligible, the perturbed wave function is given by[13]

$$\psi=\sum_{l=0}^{\infty}(2l+1)i^l\exp(i\eta_l)[\cos\eta_l\,j_l(kr)-\sin\eta_l\,n_l(kr)]\times P_l(\cos(\mathbf{k},\mathbf{r}))\,,\quad(2)$$

where j_l and n_l are the spherical Bessel and Neumann functions, respectively, P_l is a Legendre polynomial, and η_l is the lth-order phase shift for wave number k.

On substituting for ψ in Eq. (1), it can be shown that

$$\delta\rho(r)=\frac{1}{\pi^2r^2}\,\mathrm{Im}\int_0^\infty dk\,F(k)\left[e^{2ikr}\sum_{m=0}^{\infty}\left(\frac{A_m}{r^m}+i\frac{B_m}{r^m}\right)\right],\quad(3)$$

where A_m and B_m are functions of k. The coefficients A_m and B_m are given by the following expressions[14]:

$$A_{2n}=2^{-1}(2k)^{-2n}\sum_{l=0}^{\infty}(-1)^l(2l+1)\sin2\eta_l\,\Phi(l,2n)\,,$$

$$A_{2n+1}=-2(2k)^{-2n-1}\sum_{l=0}^{\infty}(-1)^l(2l+1)\sin^2\eta_l\,\Xi(l,2n+1)\,,$$

$$B_{2n}=(2k)^{-2n}\sum_{l=0}^{\infty}(-1)^l(2l+1)\sin^2\eta_l\,\Phi(l,2n)\,,$$

$$B_{2n+1}=(2k)^{-2n-1}\sum_{l=0}^{\infty}(-1)^l(2l+1)\sin(2n_l)\,\Xi(l,2n+1)\,;\quad(4)$$

where

$$\Phi(l,2n)=(-1)^n\sum_{\mu=0}^{n}\frac{(l+2\mu)!(l+2n-2\mu)!}{(2\mu)!(2n-2\mu)!(l-2\mu)!(l-2n+2\mu)!}+(-1)^n\sum_{\mu=0}^{n-1}\frac{(l+2\mu+1)!(l+2n-2\mu-1)!}{(2\mu+1)!(2n-2\mu-1)!(l-2\mu-1)!(l-2n+2\mu+1)!}\,,$$

and

$$\Xi(l,2n+1)=(-1)^n\sum_{\mu=0}^{n}\frac{(l+2\mu)!(l+2n-2\mu+1)!}{(2\mu)!(2n-2\mu+1)!(l-2\mu)!(l-2n+2\mu-1)!}\,.$$

(In evaluating A_m and B_m, it should be noted that terms containing the factorial of a negative integer in the denominator vanish.) The more important coefficients are given by the following expressions:

$$A_0=\sum_{l=0}^{\infty}(-1)^l2^{-1}(2l+1)\sin2\eta_l\,,$$

$$B_0=\sum_{l=0}^{\infty}(-1)^l(2l+1)\sin^2\eta_l\,,$$

$$A_1=-\sum_{l=0}^{\infty}(-1)^l\frac{(2l+1)(l+1)!}{(l-1)!}k^{-1}\sin^2\eta_l\,,$$

$$B_1=\sum_{l=0}^{\infty}(-1)^l\frac{(2l+1)(l+1)!}{2(l-1)!}k^{-1}\sin2\eta_l\,,$$

$$A_2=-\sum_{l=0}^{\infty}(-1)^l\tfrac{1}{8}(2l+1)\times\left[\frac{(l+2)!}{(l-2)!}+\left(\frac{(l+1)!}{(l-1)!}\right)^2\right]k^{-2}\sin2\eta_l\,,$$

$$B_2=-\sum_{l=0}^{\infty}(-1)^l\tfrac{1}{4}(2l+1)\times\left[\frac{(l+2)!}{(l-2)!}+\left(\frac{(l+1)!}{(l-1)!}\right)^2\right]k^{-2}\sin^2\eta_l\,.\quad(5)$$

If one now makes the assumption that A_m and B_m can be expanded in a Taylor's series about some appropriate point ξ in the range of integration, Eq. (3) can be expressed as

$$\delta\rho(r)=\pi^{-2}\,\mathrm{Im}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}r^{-m-2}\frac{e^{2i\xi r}}{n!}\left(\frac{\partial^nA_m}{\partial k^n}+i\frac{\partial^nB_m}{\partial k^n}\right)_\xi\times\left(\frac{1}{2i}\right)^n\frac{\partial^n}{\partial r^n}\int_0^\infty dk\,F(k)\exp[2i(k-\xi)r]\,.\quad(6)$$

The integral over k in Eq. (6) can be carried out for the four degeneracies of interest, leading to the following results:

[13] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1965), 3rd ed., p. 35.

[14] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1965), Appl. Math. Ser. 55.

1. Slight degeneracy. When $\beta^2 k_T^2 \gtrsim 0$, where $\beta^2 = \hbar^2/(2m^* k_B T)$, $F(k)$ can be expanded in powers of $\exp[\beta^2(k^2 - k_T^2)]$ in the range $k^2 < k_T^2$, and in powers of $\exp[-\beta^2(k^2 - k_T^2)]$ in the range $k^2 > k_T^2$. It can then be shown that

$$\int_0^\infty dk\, F(k) e^{2ikr} = \frac{i}{2r} - e^{2ik_T r}\left\{ i/2r + \sum_{\lambda=1}^{\infty} (-1)^\lambda \frac{1}{2}\left(\frac{\pi}{\lambda}\right)^{1/2} \frac{1}{\beta} \times [\exp(\nu_\lambda^2)\,\mathrm{erfc}(\nu_\lambda) + i\exp(\omega_\lambda^2)\,\mathrm{erfc}(\omega_\lambda) - iW_\lambda] \right\}, \quad (7)$$

where $\nu_\lambda = \lambda^{1/2}\beta k_T - \lambda^{-1/2} i\beta^{-1} r$, $\omega_\lambda = \lambda^{-1/2}\beta^{-1} r - \lambda^{1/2} i\beta k_T$, erfc denotes an error function,[14] and

$$W_\lambda = \exp(\omega_\lambda^2)\,\mathrm{erfc}(\lambda^{-1/2}\beta^{-1} r).$$

In the limit $\beta k_T \gg 1$, Eq. (7) can be shown to reduce to the relation

$$\int_0^\infty dk\, F(k) e^{2ikr} \approx \frac{i}{2r} + \tfrac{1}{2}\pi^{1/2} \frac{i}{\beta} e^{2ik_T r} \sum_{\lambda=1}^{\infty} (-1)^\lambda \lambda^{-1/2} W_\lambda - \frac{\pi i}{2\beta^2 k_T} e^{2ik_T r}\,\mathrm{csch}\frac{\pi r}{\beta^2 k_T}. \quad (8)$$

It is convenient at this stage to replace ξ by 0. On substituting for the integral in Eq. (6) from Eq. (8) and invoking the property that for k small A_m and B_m can be expressed in odd and in even powers of k, respctively,[15] the term $i/2r$ and terms containing W_λ disappear. One obtains then through a Taylor's expansion the result

$$\delta\rho(r) = -\frac{1}{2\pi\beta^2 k_T} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} (-\tfrac{1}{4})^n \frac{Q_{mn}}{r^{m+2}} \cos(2kr + v_{mn}), \quad (9)$$

where

$$Q_{mn}\cos v_{mn} = \left(\frac{1}{(2n)!} \frac{\partial^{2n} A_m}{\partial k^{2n}} \frac{\partial^{2n}\chi}{\partial r^{2n}} + \frac{1}{2(2n+1)!} \frac{\partial^{2n+1} B_m}{\partial k^{2n+1}} \frac{\partial^{2n+1}\chi}{\partial r^{2n+1}} \right)_{k_T},$$

$$Q_{mn}\sin v_{mn} = \left(\frac{1}{(2n)!} \frac{\partial^{2n} B_m}{\partial k^{2n}} \frac{\partial^{2n}\chi}{\partial r^{2n}} - \frac{1}{2(2n+1)!} \frac{\partial^{2n+1} A_m}{\partial k^{2n+1}} \frac{\partial^{2n+1}\chi}{\partial r^{2n+1}} \right)_{k_T},$$

$\chi = \mathrm{csch}(\pi r/\beta^2 k_T)$, $k_T = k_0 - \Delta k$, with k_0 denoting the Fermi wave number at absolute zero, and $\Delta k \approx \pi^2/(24\beta^4 k_0^4)$ is the blurring of the Fermi level due to thermal excitations.[16] [It should be pointed out that Eq. (9) can equally well be obtained by replacing ξ by k_T in Eq. (6).[17] The derivation tends, however, to be more laborious than when $\xi = 0$.] Expressions (6b) of Flynn and Odle[6] and (5.5) of Adawi[7] can be immediately related to the first term of Eq. (9) (i.e., when m and n are equated to zero) with the appropriate values given to A_0 and B_0.

Within the range $r < \beta^2 k_T$, an expansion of $\mathrm{csch}(\pi r/\beta^2 k_T)$ in powers of T can be utilized to express Eq. (9) in a very useful form

$$\delta\rho(r) = -\frac{1}{2\pi^2} \sum_{\lambda=0}^{\infty} \left(\frac{C_\lambda \cos(2kr + \phi_\lambda)}{r^{\lambda+3}} - \Omega T^2 \frac{D_\lambda \cos(2kr + \zeta_\lambda)}{r^{\lambda+1}} + O(T^4)\cdots \right)_{k=k_T}, \quad (10)$$

where

$$C_\lambda \cos\phi_\lambda = \sum_{\mu=0}^{\lambda} (-\tfrac{1}{4})^\mu \left(\frac{\partial^{2\mu} A_{\lambda-2\mu}}{\partial k^{2\mu}} - \frac{1}{2} \frac{\partial^{2\mu+1} B_{\lambda-2\mu-1}}{\partial k^{2\mu+1}} \right),$$

$$C_\lambda \sin\phi_\lambda = \sum_{\mu=0}^{\lambda} (-\tfrac{1}{4})^\mu \left(\frac{\partial^{2\mu} B_{\lambda-2\mu}}{\partial k^{2\mu}} + \frac{1}{2} \frac{\partial^{2\mu+1} A_{\lambda-2\mu-1}}{\partial k^{2\mu+1}} \right),$$

$$D_\lambda \cos\zeta_\lambda = A_\lambda + \tfrac{1}{2}\partial B_{\lambda-1}/\partial k,$$

$$D_\lambda \sin\zeta_\lambda = B_\lambda - \tfrac{1}{2}\partial A_{\lambda-1}/\partial k,$$

and

$$\Omega = \tfrac{2}{3}(\pi m^* k_B)^2/\hbar^4 k_T^2.$$

In evaluating Eq. (10), A_ν, B_ν, and their derivatives are equated to zero when the integer subscript ν is negative.

2. Complete degeneracy. For a completely degenerate electron gas (i.e., $\beta k_T \to \infty$) it can be shown that

$$(\pi/\beta^2 k_T)\,\mathrm{csch}(\pi r/\beta^2 k_T) \to 1/r. \quad (11)$$

The density, as given by Eq. (9), reduces in this case to the expression

$$\delta\rho(r) = -\frac{1}{2\pi^2} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} (-\tfrac{1}{4})^n r^{-m-2n-3} \times \left[(\cos 2kr)\left(\frac{\partial^{2n} A_m}{\partial k^{2n}} - \frac{1}{2r} \frac{\partial^{2n+1} B_m}{\partial k^{2n+1}} \right) - (\sin 2kr)\left(\frac{\partial^{2n} B_m}{\partial k^{2n}} + \frac{1}{2r} \frac{\partial^{2n+1} A_m}{\partial k^{2n+1}} \right) \right]_{k_0}. \quad (12)$$

This equation can be written in the more compact form

$$\delta\rho(r) = -\frac{1}{2\pi^2} \sum_{\lambda=0}^{\infty} C_\lambda r^{-\lambda-3} \cos(2kr + \phi_\lambda), \quad (13)$$

---

[15] N. F. Mott and H. S. M. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1965), 3rd ed., p. 45.

[16] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Co., New York, 1960), p. 149.

[17] A. Sommerfeld and H. Bethe, in *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Springer-Verlag, Berlin 1934), Vol. XXIV.

where C_λ and ϕ_λ are defined in Eq. (10), and $k=k_0$. It is again of interest to point out that the first two terms of Eq. (13) correspond to Eq. (4) of Alfred and Van Ostenburg[8] with A_0, B_0, A_1, and B_1 defined in Eq. (5). Friedel's[3] Eq. (11) for a thin spherical well is obtained when $C_1/C_0=2k_0$, $\phi_0=0$, and $\phi_1=\pi/2$.

3. Intermediate degeneracy. By utilizing a series representation for the error function, Eq. (7) can be expressed as[6]

$$\int_0^\infty dk\,F(k)e^{2ikr}=\frac{i}{2r}+\frac{i}{\beta}e^{2ik_Tr}\left(\sum_{\lambda=1}^{\infty}(-1)^\lambda\frac{1}{2}\left(\frac{\pi}{\lambda}\right)^{1/2}W_\lambda\right.$$
$$\left.-\pi\sum_{\mu=0}^{\infty}\frac{i^\mu}{\mu!(2\beta k_T)^{2\mu+1}}\frac{\partial^{2\mu}}{\partial y^{2\mu}}(y^\mu\,\mathrm{csch}\pi y)\right),\quad(14)$$

where $y=r/\beta^2k_T$. On substituting the above expression for the integral in Eq. (6), one obtains the result

$$\delta\rho(r)=-\frac{1}{\pi}\,\mathrm{Im}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}(-1)^n\beta^{-n-1}r^{-m-2}$$
$$\times\frac{e^{2ik_Tr}}{n!}\left(\frac{\partial^nA_m}{\partial k^n}+i\frac{\partial^nB_m}{\partial k^n}\right)_{k_T}$$
$$\times\sum_{\mu=0}^{\infty}\frac{i^{\mu+n+1}}{\mu!(2\beta k_T)^{2\mu+n+1}}\frac{\partial^{2\mu+n}}{\partial y^{2\mu+n}}(y^\mu\,\mathrm{csch}\pi y),\quad(15)$$

where ξ has been replaced by 0. The term $i/2r$ and terms containing W_λ do not appear (see the case of slight degeneracy above) in Eq. (15).

The expansion of $\mathrm{csch}\pi y$ in powers of $e^{-\pi y}$ can now be used to establish the following relation:

$$\frac{\partial^s}{\partial y^s}(y^\mu\,\mathrm{csch}\pi y)=2(-\pi)^{s-\mu}\mu!\sum_{\nu=0}^{\infty}(2\nu+1)^{s-\mu}$$
$$\times e^{-(2\nu+1)\pi y}L_\mu{}^{s-\mu}[(2\nu+1)\pi y],\quad(16)$$

where $s>\mu$, and $L_\mu{}^{s-\mu}$ is an associated Laguerre polynomial.[14] With the help of Eq. (16) the derivatives of $y^\mu\,\mathrm{csch}\pi y$ appearing in Eq. (15) can be replaced by more tractable expressions. Thus for $y\gg1$ the first term of the summation in Eq. (16) is a good approximation. When y is not large, however, higher-order terms of the summation have to be considered. When $\beta k_T>1$, the right-hand side of Eq. (15) can be treated as a series in inverse powers of βk_T; fewer terms of the series need to be considered as βk_T gets larger. In the limit of $\beta k_T\gg1$, which corresponds to the case of screening in a slightly degenerate electron gas, Eq. (15) reduces to Eq. (9), as expected.

It is of interest to point out that Eq. (6a) of Flynn and Odle[6] can be obtained from Eqs. (15) and (16), when $m=0$, $n=0$, $y\gg1$, and assuming that terms of order $<\mu$ can be neglected in $L_\mu{}^\mu(\pi y)$.

4. Nondegeneracy. When $\beta^2k_T^2$ is negative, it can be shown that

$$\int_0^\infty dk\,F(k)e^{2ikr}=\sum_{\mu=1}^{\infty}(-1)^{\mu+1}\frac{\sqrt{\pi}}{2(\sqrt{\mu})\beta}$$
$$\times e^{\mu\beta^2k_T^2-r^2/\mu\beta^2}\,\mathrm{erfc}\frac{-ir}{(\sqrt{\mu})\beta}.\quad(17)$$

On substituting this result in Eq. (6) one obtains for the long-range screening density in a nondegenerate electron gas the expression

$$\delta\rho(r)=\frac{1}{\pi^{3/2}}\sum_{m=0}^{\infty}\sum_{\lambda=0}^{\infty}\sum_{\mu=1}^{\infty}r^{-m-2}\exp(\mu\beta^2k_T^2-r^2/\mu\beta^2)$$
$$\times(-1)^\lambda\left[\frac{1}{(2\lambda+1)!}\left(\frac{1}{2(\sqrt{\mu})\beta}\right)^{2\lambda+2}\left(\frac{\partial^{2\lambda+1}A_m}{\partial k^{2\lambda+1}}\right)_{k=0}\right.$$
$$\times H_{2\lambda+1}\left(\frac{r}{(\sqrt{\mu})\beta}\right)+\frac{1}{(2\lambda)!}\left(\frac{1}{2(\sqrt{\mu})\beta}\right)^{2\lambda+1}$$
$$\left.\times\left(\frac{\partial^{2\lambda}B_m}{\partial k^{2\lambda}}\right)_{k=0}H_{2\lambda}\left(\frac{r}{(\sqrt{\mu})\beta}\right)\right],\quad(18)$$

where H_n denotes a Hermite polynomial,[14] and ξ has been equated to 0.

Equation (18) reduces to a simple form in the following special cases:

(a) For r/β small, and $|\beta^2k_T^2|$ large,

$$\delta\rho(r)\approx(2\pi^{3/2}\beta^3)^{-1}\exp(\beta^2k_T^2-r^2/\beta^2)$$
$$\times\sum_{m=0}^{\infty}r^{-m-1}\left[\frac{\partial A_m}{\partial k}+\frac{\partial^2B_m}{\partial k^2}\left(\frac{1}{4r}-\frac{r}{2\beta^2}\right)\right]_{k=0},\quad(19)$$

where the dominant term is effectively Coulombic.

(b) For $r<2\beta^2$, $T<1000°$K, and $|\beta^2k_T^2|$ large,

$$\delta\rho(r)\approx(2\pi^{3/2}\beta^3)^{-1}\left(\frac{\partial A_0}{\partial k}\right)_{k=0}r^{-1}\exp\left(\beta^2k_T^2-r^2/\beta^2\right),\quad(20)$$

which corresponds to Eq. (5) of Kochelaev[9] when the approximation $\eta_0\propto k$ is employed to determine A_0.

(c) For $r>2\beta^2$ and $|\beta^2k_T^2|$ large, the higher terms with index λ and m in Eq. (18) are important, as $H_n(x)\to x^n$ for $x\gg1$. The number of terms in the series will be small if the higher derivatives of A_m and of B_m at $k=0$ are negligible.

B. Screening Potential around a Localized Point Charge

The self-consistent potential $V(r)$, corresponding to the density in the four degeneracy cases considered above, can be derived from the integral form of Poisson's

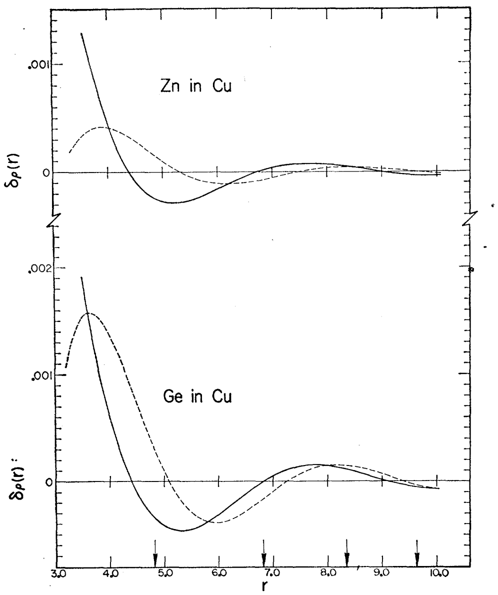

FIG. 1. Density of the screening charge cloud $\delta\rho(r)$ around an impurity atom in Cu at 1000°C. Dashed line, Friedel wiggle; solid line calculated from Eq. (10) and from Ref. 5. Arrows indicate position of nearest neighbors. Atomic units are used.

equation:

$$V(r)=-\frac{4\pi e_c}{\kappa r}\int_r^\infty r^2\delta\rho(r)dr+\frac{4\pi e_c}{\kappa}\int_r^\infty r\delta\rho(r)dr, \quad (21)$$

where κ is the dielectric constant, e_c is the charge of a carrier, and $\delta\rho(r)$ is the appropriate carrier-density expression. The integrals in Eq. (21) can be evaluated quite conveniently by parts, treating the circular functions as the integrable part of the integrand when $\delta\rho(r)$ is given by Eqs. (9), (10), (13), and (15), and the inverse power of r as the differentiable part when it is given by Eq. (18). In the important case of screening in a slightly degenerate gas [corresponding to Eq. (10)], the potential is given by

$$V(r)=\frac{2e_c}{\pi\kappa}\sum_{\lambda=0}^{\infty}\left(\frac{C_\lambda Y_\lambda}{r^{\lambda+1}}\cos(a_\lambda+\phi_\lambda)\right.$$
$$\left.-\Omega T^2\frac{D_\lambda Y_{\lambda-2}}{r^{\lambda-1}}\cos(a_{\lambda-2}+\zeta_\lambda)+O(T^4)\cdots\right)_{k=k_T}, \quad (22)$$

where

$$Y_\nu\cos a_\nu=\mathrm{Ci}_{\nu+1}(2kr)-\mathrm{Ci}_{\nu+2}(2kr),$$
$$Y_\nu\sin a_\nu=\mathrm{Si}_{\nu+1}(2kr)-\mathrm{Si}_{\nu+2}(2kr),$$

Ci_μ and Si_μ are generalized cosine and sine integrals,[18] respectively; ν and μ denote integers. In expressing the result in terms of the generalized cosine and sine integrals it has been assumed that there is no significant error in changing the upper limit of the integrals in Eq. (21) to $r\approx\beta^2k_T$. Also, since $\rho(r)$ and $V(r)$ are well-behaved functions for $r\to\infty$, Ci_{-1} and Si_{-1} denote values of the integral at the lower limit of integration.

In the case of screening in a completely degenerate electron gas the potential can be obtained from Eq. (22) by retaining the first term in the large parentheses and replacing k_T by k_0. For the other degeneracies the expression for the potential is rather cumbersome. There is not much point in presenting their explicit form since, as indicated above, they can be obtained without difficulty.

III. DISCUSSION

In the case of screening in a slightly degenerate electron gas, it is of interest to compare the screening density, as given by Eq. (9) or (10), with that given by the Friedel wiggle (r^{-3} term). For impurity screening in copper at 1000°C, it is found that the deviations from the expression of Friedel are of the order of 10% at the first neighbors, when the first-order perturbation result[10]: $A_0\propto k_0(1+2\pi k_0)^{-2}$ is adopted. The deviations are much greater (see Fig. 1) when phase shifts obtained from a semiempirical scheme[5,19] or a square-well potential[20] are utilized in Eq. (4). In general, it is found that the asymptotic screening field in a slightly degenerate electron gas, as given by Eq. (9) or (10), oscillates in a much more complex way than suggested by the Friedel form. In fact, it can be shown that the elementary expression in r^{-3} is applicable only at very large values of r in a completely degenerate electron gas. For all other situations it is a rough approximation. The main corrections to the Friedel expression are found to arise from terms in higher powers of r^{-1} at ordinary lattice temperatures. Since Δk is usually small for $T<10^4$°K, corrections due to temperature only are almost negligible within that temperature range.

By merely inspecting the functional form of Eq. (9), one can see that the temperature enters the screening field in the slightly degenerate electron gas through factors of the form $\beta^{-2}k_T^{-1}\,\mathrm{csch}(\pi\beta^{-2}k_T^{-1}r)$ and its derivatives with respect to r. It can also be noted that at absolute zero the field reduces to the product of a circular function and of a series in inverse powers of r; the first term of that series corresponding to the Friedel wiggle. One should be cautioned, however, against attempting to determine by inspection the relative importance of the terms in Eqs. (9) or (10) at the first- and second-neighbor distance. Since the higher derivatives of the phase shifts or of A_m and B_m can get quite large, higher-order terms in the series may turn out to be of comparable magnitude to the Friedel oscillations.

Apart from sinusoidal-type oscillations, there are no outstanding features in the screening field for the electron gas of intermediate degeneracy. The expression

[18] R. B. Dingle, Appl. Sci. Res. **B4**, 411 (1955).

[19] L. C. R. Alfred and D. O. Van Ostenburg, Phys. Rev. **161**, 569 (1967).

[20] F. J. Blatt, Phys. Rev. **108**, 285 (1957).

for the screening charge density is slightly more complicated in this case than it is in the slightly degenerate electron gas. The temperature dependence, which is significant here, shows up as factors of the form $\beta^{-1}(\beta k_T)^{-2\mu-1}\exp[-(2\nu+1)\pi y]L_\mu{}^\mu[(2\nu+1)\pi y]$, where μ and ν are integers, and its derivatives with respect to r. For very large values of r the field keeps oscillating and drops off roughly[6] as the product of a circular function with argument $(2+\pi^2/4\beta^4k_T{}^4)k_Tr$, of $e^{-\pi y}$, and of a series in inverse powers of r. An expression corresponding to the Friedel wiggle is always present in the screening field for the intermediate-degeneracy case. It is only in the high degeneracy limit, however, that it becomes an important term.

One of the interesting characteristics in the asymptotic form of the screening field in the nondegenerate electron gas is the absence of the sinusoidal-type oscillations observed in the degenerate cases. This has been attributed[7] to the blurring of the Fermi surface. In the present analysis the oscillations vanish because the circular terms in Eqs. (9), (13), and (15) arise from an integration over a range $0\leq k\leq \mathrm{Re}\beta k_T$, which is nonexistent in the nondegenerate electron gas. Some waviness in the screening field will be observed, however, in the range $r<2\beta$, on account of the dependence on Hermite polynomials. Although the screening field in the nondegenerate gas does not display the spectacular features found in the degenerate cases, its functional variation with distance and temperature is just as complex. Simple function forms are obtainable only in some limiting cases. Thus, a Gaussian dependence with argument $\beta^{-1}r$ is valid in the range $r<2\beta^2$; $T<1000$°K. A Coulombic dominant term in the screening field can also be obtained when the conditions $r<\beta$, $|\beta^2k_T{}^2|\gg 1$ are satisfied. No relationship to the Brooks-Herring screened Coulomb is indicated, however, at any distance or temperature range for the nondegenerate case in the present scheme.

It is of interest to compare the results obtained for long-range screening in an electron gas by the present method with results of previous work. Since the present approach is an extension of that utilized by Flynn and Odle,[6] there are many points of similarity in the expressions derived in the two investigations. The results presented here, however, are in a much more general form and have a broader scope than those of the above-mentioned authors. The screening fields obtained by Adawi[7] and others[9,10] through inversion of the Hartree dielectric constant are severely restricted by the approximations that must be made to obtain analytical solutions. It is also well known that important details of the fine structure of the screening field cannot be resolved in a first-order-perturbation approach. Furthermore, the results of Langer and Vosko,[10] unlike those of the present investigation, cannot be utilized in higher-order approximations or with semiempirical parameters.

A very plain framework has been considered in the present investigation, and it is appropriate to comment briefly on the main shortcomings of the model and on the refinements that should be considered for a more rigorous treatment. One of the simpler corrections pertains to the deviation of the actual wave function ψ, in Eq. (1), from the simple form given by Eq. (2). This refinement could be significant in the immediate neighborhood of the potential cutoff, i.e., at the first few neighbors in common metal lattices. The present scheme [Eq. (1)] can be utilized for this modification provided the deviations of the wave functions are known. Next, one must consider the standard refinements to the primitive free-electron scheme. The most important of these involve taking proper account of the Bloch character of the charge carriers, of exchange, and of phonon interaction. These three modifications, however, unlike the one discussed above, cannot be incorporated readily within the present scheme and are meant for more powerful many-body and band-structure techniques. Other important corrections relate to nonspherical Fermi surfaces and realistic ionic cores. These two refinements are known to be quite complex even at absolute zero. Introducing them in the screening scheme for arbitrary temperatures will clearly present major difficulties.

IV. CONCLUSIONS

The main conclusions emerging from the present investigation are the following.

(1) In the case of screening in a slightly degenerate or completely degenerate electron gas, higher-order corrections in powers of r^{-1} to the Friedel oscillations are very important and cannot be neglected in discussing short range interaction between an impurity atom and the matrix, or in constructing a pair potential in liquid metals.

(2) Since the blurring of the Fermi surface Δk due to thermal excitations is small at temperatures of the order of 1000°C, corrections to k_0 and to the phase shifts due to temperature only are not significant in the common metals up to temperatures well past the melting point. Consequently, there is no significant error in evaluating the screening field over that temperature range with parameters obtained at absolute zero. There is also complete agreement with the observation of Flynn and Odle[6] to the effect that, within the limitations of the present model, many physical properties of dilute alloys should be temperature-invariant.

(3) In the case of screening in a nondegenerate electron gas the sinusoidal-type oscillations observed in the degenerate cases are absent. The field varies with distance, temperature, and the Fermi-Dirac normalizing parameter in a very complex way. Simple forms like a Gaussian or a Coulomb dependence are obtainable as limiting cases and they can be utilized only within their range of validity.

(4) Since the expressions obtained for the screening field are presented here in their most general form, they

tend to appear cumbersome and inconvenient for practical applications. In practice, however, only the first few terms in the summations will be significant. The number of these terms will clearly vary with the distance and temperature range under consideration and also with the convergence pattern of the coefficients in the series.

(5) The results of the present investigation give a more comprehensive and unified picture of some aspects of the charge-screening problem in an electron gas than has yet been presented. They should be extremely useful in a wide range of problems, particularly those where elementary asymptotic field, such as the Friedel wiggle, are being employed. They should also serve as a useful first approximation in more sophisticated treatments of long-range charge screening in an electron gas.

PHYSICAL REVIEW VOLUME 185, NUMBER 3 15 SEPTEMBER 1969

Specific Heat of *n*- and *p*-Type Bi_2Te_3 from 1.4 to 90°K*

G. E. SHOEMAKE† AND J. A. RAYNE
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

AND

R. W. URE, JR.‡
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235

(Received 4 March 1969)

The specific heats of *n*-type bismuth telluride with carrier concentrations ranging between 2.2×10^{18} and 8.3×10^{20} cm^{-3}, *p*-type Bi_2Te_3 with a carrier concentration of 1.3×10^{19} cm^{-3}, and bismuth selenide have been measured from 1.3 to 90°K. At low temperatures, there are measurable differences in the electronic specific heat of *n*-type Bi_2Te_3 as a function of carrier concentration. These differences can be explained on the basis of a conduction band consisting of six ellipsoidal minima and an additional heavy-mass band lying approximately 30 meV above them. The electronic specific heat of *p*-type Bi_2Te_3 is consistent with a six-ellipsoid model. For both *n*- and *p*-type Bi_2Te_3, as well as Bi_2Se_3, departure of the lattice specific heat from the Debye T^3 approximation begins well below the lowest temperatures measured. The extrapolated Debye temperature at absolute zero is (162 ± 3)°K for Bi_2Te_3, which agrees well with the value of (165 ± 2)°K obtained from the low-temperature elastic constants. Bi_2Se_3 has been found to have a limiting Debye temperature of (182 ± 3)°K.

I. INTRODUCTION

WITHIN the last ten years, a significant amount of progress has been made towards an understanding of the transport properties of Bi_2Te_3 in terms of an ellipsoidal multivalley model for its conduction and valence bands.[1,2] Recent de Hass–van Alphen studies,[3,4] together with related transport measurements on *n*-type Bi_2Te_3,[5] have led to the postulates of an additional heavy-mass low-mobility conduction band lying at a slightly higher energy than the ellipsoidal minima. The existence of such a band can be checked directly by examining the behavior of the electronic specific heat. Although specific-heat measurements have been made previously on Bi_2Te_3, none have been obtained for *n*-type material and indeed the electronic specific heat of *p*-type Bi_2Te_3 appears to be in serious disagreement with that calculated from the results of de Haas–van Alphen (dHvA) measurements. This work then is primarily concerned with an experimental determination of the specific heat of *n*-type Bi_2Te_3 to deduce information concerning the second band, and with a remeasurement of the electronic heat capacity of *p*-type material. Of interest, too, is the limiting Debye temperature Θ_0, which can be compared with Θ_0 calculated from elastic constants, and the variation of the lattice heat capacity with temperature and doping impurities. The specific heat of bismuth selenide has also been measured to observe the difference in lattice heat capacity caused by the substitution of selenium for tellurium.

* Work supported by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force Grant No. AF-AFOSR-870-65. This paper is based on a thesis submitted by one of us (GES) as partial fulfillment of the requirements for the Ph.D. degree in Physics at Carnegie-Mellon University.

† Present address: General Dynamics, Fort Worth, Tex.

‡ Present address: College of Engineering, University of Utah, Salt Lake City, Utah, 84112.

[1] J. R. Drabble, in *Progress in Semiconductors*, edited by A. E. Gibson and R. E. Burgess (Wiley-Interscience, Inc., New York, 1963), Vol. 7, p. 47.

[2] H. J. Goldsmid, J. Appl. Phys. Suppl. **32**, 2198 (1961).

[3] R. B. Mallinson, J. A. Rayne, and R. W. Ure, Jr., Phys. Letters **24A**, 713 (1967).

[4] R. B. Mallinson, J. A. Rayne, and R. W. Ure, Jr., Phys. Rev. **175**, 1049 (1968).

[5] R. W. Ure, Jr., in *International Conference on the Physics of Semiconductors, Exeter, 1962* (Institute of Physics and Physical Society, London, 1962), p. 659; Y. Yates, J. Electronics Control **6**, 26 (1959); P. A. Walker, Proc. Phys. Soc. (London) **76**, 113 (1960).