

Screening in Dilute Alloys and Dilute Metals in the Light of Solutions of the Nonlinear Thomas-Fermi Equation*

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A practical procedure has been developed for solving the nonlinear Thomas-Fermi equation by quadrature, and has been applied to screening problems in dilute alloys and dilute metals. For the dilute-alloy problem, results of calculations are presented in curves and equations for factors for the effective charge of impurity ions which can be applied to any alloy system of interest. In the case of dilute metals, the effect of the gradual localization of charge as the atomic radius r_0 per metal atom is increased was studied. The model allows for the presence of a matrix of other atoms or molecules through a dielectric constant K and effective mass ratio M . Also, it is necessary to take into account the exclusion of the valence electrons from the ion core region. This is done by means of an ion core radius r_c , within which the band electrons are excluded. Calculations were made for two effective mass ratios μ_0 and μ_1 , which measure the effect of charge localization, respectively, in reducing the Fermi energy and in reducing the density of states at the Fermi energy. In addition to the dependence on r_0 and r_c , the ratios μ_0 and μ_1 depend on the "reduced" charge Z_1 , which is the charge of the metal ion multiplied by $(M/K)^3$. The implication of the results for these models is discussed for screening as it actually occurs in dilute alloys and in dilute metals.

I. INTRODUCTION

THE Thomas-Fermi (TF) equation has been a useful source of information about the distribution of valence-electron charge in alloys. A detailed study of its implications in dilute alloys has been made by Friedel,¹ largely in the context of the solution of the linearized equation. The effect of an impurity with a charge Z' (difference between the ionic charge of impurity and host atoms) is to cause an excess electron density $\delta n(r)$ centered on the impurity ion and a shift in the Fermi energy E_F from the value E_{F0} for the pure solute. The latter is associated with a nonzero value of δn at r_0 , the radius of the spherical volume per impurity atom. Friedel showed that $\delta n(r_0)$ rapidly approaches zero when r_0 is large compared to the screening distance λ . Since $\delta n(r_0)$ is proportional to Z' in the linearized solution, this result is conveniently described in terms of the effective charge of the impurity $z = \frac{4}{3}\pi r_0^3 \delta n(r_0)$. The ratio $\alpha_1 = z/Z'$ is a simple function $f(r_0/\lambda)$; f approaches unity for $r_0 < \lambda$, and it approaches zero for $r_0 > \lambda$. (The subscript 1 on α denotes the value in the linear approximation.)

Linearization of the TF equation depends on the assumption that the potential energy $V(r)$ is small compared to E_F . This is a poor approximation in most metals, and it has been long recognized that the linearized solution is inaccurate. Friedel¹ considered the effect of next-order terms, which has an advantage mainly in giving a qualitative understanding of the effect of the nonlinearity: α is smaller than α_1 for $Z' > 0$, and larger for $Z' < 0$. Accurate calculations for the nonlinear effect were obtained by Alfred and March for impurities in copper² and Fujiwara for impurities in silver.³ Using numerical methods, they obtained

accurate solutions for $Z' > 0$; these are conveniently expressed in terms of a ratio α/α_1 which we will refer to as β . Alfred and March also obtained approximate solutions for β for Ag and Cu for $Z < 0$.⁴

The main difficulty in numerically integrating the (second-order) nonlinear TF equation develops from the fact that the known information for a given problem provides input data for one boundary condition at each end of the range of integration: $dV/dr = 0$ at $r = r_0$, and $dV/dr = +2Z/r^2$ at $r \rightarrow 0$. (We will use atomic units throughout this paper.) Alfred and March⁴ and Fujiwara met this difficulty by using a relaxation method, which leads to the necessity of solving a matrix equation whose order must be increased for increasing accuracy of solution. A much simpler numerical solution can be obtained directly by the method of quadrature if one assumes various values of E_F and determines $Z'(E_F)$ which arises from the calculated value of dV/dr at $r = 0$. Inversion of this function yields E_F at various values of Z' . This approach is well suited for the use of high-speed computers.

It is possible to lump together the various fixed constants (Z', r_0, E_{F0}) in such a way that β can be expressed as a single function of the combined parameters for any particular value of r_0/λ . (A different function is necessary for positive and negative Z' .) We find, as one might expect, that these curves asymptotically approach a single one for large r_0/λ . Since r_0/λ is large for even fairly concentrated alloys, this limit is effectively a single solution which is invariant with impurity concentration. These results represent a considerable extension of the results of Alfred and March, and Fujiwara, since they are applicable to any dilute-alloy system, within the limitations of the physical accuracy of the original nonlinear TF equation. For convenience in making use of

* Work supported by the U. S. Atomic Energy Commission.

¹ J. Friedel, *Advan. Phys.* **3**, 446 (1954).

² L. C. R. Alfred and N. H. March, *Phil. Mag.* **46**, 759 (1955).

³ H. Fujiwara, *J. Phys. Soc. Japan* **10**, 339 (1955); **10**, 727 (1955).

⁴ L. C. R. Alfred and N. H. March, *Phys. Rev.* **103**, 877 (1956). In a later paper [*Phil. Mag.* **2**, 985 (1957)] a more accurate solution was obtained for $Z' < 0$, but the result was not expressed in terms of β .

the calculated asymptotic curves, they have been put in an analytic form by means of a least-squares fit to an arbitrary function with an appropriate number of adjustable constants.

Our original interest in solving the nonlinear TF equation stems from an interest in dilute metals rather than dilute alloys. By dilute metals, we mean systems in which there is an electronic conduction band which contains a small density of electrons compared to metals, but for which the corresponding positive charge is localized, rather than diffuse as in typical semimetals (e.g., bismuth). Our own interest is in liquid semiconductors, *n*-type thallium-tellurium⁵ in particular, but many other systems meet this definition; for instance, concentrated solutions of alkali metals in liquid ammonia, or tungsten bronzes. The nature of the electronic structure and electronic transport in these systems is not well understood and is a subject of considerable research interest.⁶

It is evident that there will be a considerable localization of electronic charge in the vicinity of the positive ions in dilute metals. At low enough concentrations, it is believed that an abrupt transition to an insulator state where the electrons are fully localized—the Mott transition—will occur.⁷ But in the intermediate range between the metallic and insulating states, the partial localization should develop continuously in the sense described so well by Friedel for alloys.¹ This may be profitably examined in terms of the solution of the TF equation.

In doing this, one must recognize a number of differences from the dilute alloy problem: (1) Since the Fermi energy is smaller and the screening distance larger (though smaller compared to r_0), the linear approximation is impossibly bad. (2) The considerations, by which one is led to deal with $\delta n(r)$, and to let Z' equal the difference in charge between impurity and solute ions, do not apply in dilute metals. One must instead consider the total density of valence electrons $n(r)$ in the field of a positive ion whose charge Z is the total ionic charge. r_0 becomes the radius of the spherical volume per ion. (3) Dilute metals are usually stable only in the presence of a matrix of other atoms which might be assumed to act as a dielectric medium. An exception to this is provided by metallic vapors at high density, as occurs, for instance, in recent studies of mercury.⁶ Therefore, one should incorporate a dielectric constant K in the TF equation. Also one should include an effective mass factor M . These factors are justified rigorously only at the extreme of low electron concentrations, and then perhaps only in crystalline materials. The proper description of what goes on between these densities and metallic densities is not clear. In the framework of the

simple TF equations, K and M are arbitrary constants which may vary with electron concentration. Some of the implications of this point of view will be discussed later.

The solutions for the dilute metal can be examined in terms of the behavior of the E_F as a function of Z and r_0 . It is observed, as expected, that the ratio of E_F to the free-electron value E_{F0} decreases rapidly as r_0 increases. The Fermi-energy effective-mass ratio E_{F0}/E_F , which we call μ_0 , is not as significant as another effective mass associated with the density of states at the Fermi energy, which we call μ_1 . μ_1 appears in most formulas describing the electronic behavior of metallic or semi-metallic systems. Both of these are calculated as a function of r_0 and Z .

For small r_0 , approaching metallic concentrations, one would expect μ_0 and μ_1 to have values associated with typical metals. Solutions of the nonlinear equation along the lines described above do not give this result, and the reason is soon evident. In real metals, the valence-electron density drops to very low values within the ion core region because the wave functions must be orthogonal to those of the core electrons. As a result of the nonlinear character of the solution a very significant fraction of the electronic charge in the TF solution is within the core region, notwithstanding the relatively small volume. It has been established in other studies that a fair representation of many aspects of the behavior of metals can be deduced from models in which the electron density is arbitrarily made equal to zero within an arbitrary core radius r_c , which is usually treated as an empirically determined parameter.⁸ We make this assumption in calculating solutions for the dilute metals, and find that solutions for metallic concentrations then become physically reasonable.

II. DILUTE ALLOYS

The basic equations for dilute alloys are (in a. u.)

$$\nabla^2 V(r) = -8\pi\delta n(r), \quad (1a)$$

$$\delta n(r) = [\{E_F - V(r)\}^{3/2} - E_{F0}^{3/2}]/3\pi^2. \quad (1b)$$

The boundary conditions are

$$V = dV/dr = 0, \quad \text{at } r = r_0 \quad (2a)$$

$$dV/dr = 2Z'/r^2, \quad \text{at } r \rightarrow 0 \quad (2b)$$

where $\frac{4}{3}\pi r_0^3$ is equal to the volume per impurity atom.

The variable $V(r)$ is normalized to $v(r) = V(r)/E_{F0}$, and the corresponding normalized Fermi energy is $\epsilon = E_F/E_{F0}$. For convenience in carrying out integrations, we use the variable $w = vx\rho_0$. This leads to the equation

$$d^2w/dx^2 = -(\frac{2}{3}\rho_0^3x)[(\epsilon - w/x\rho_0)^{3/2} - 1], \quad (3a)$$

⁵ M. Cutler and M. B. Field, Phys. Rev. **169**, 632 (1968).

⁶ A good review of the subject, with many references, is given by N. F. Mott, Advan. Phys. **16**, 49 (1967).

⁷ N. F. Mott, Proc. Phys. Soc. (London) **A62**, 416 (1949); Can. J. Phys. **34**, 1356 (1956); Phil. Mag. **6**, 287 (1961).

⁸ J. C. Raich and R. H. Good, Jr., J. Phys. Chem. Solids **26**, 1061 (1965); M. Cutler, J. Chem. Phys. **46**, 2044 (1967); N. W. Ashcroft and D. C. Langreth, Phys. Rev. **155**, 682 (1967).

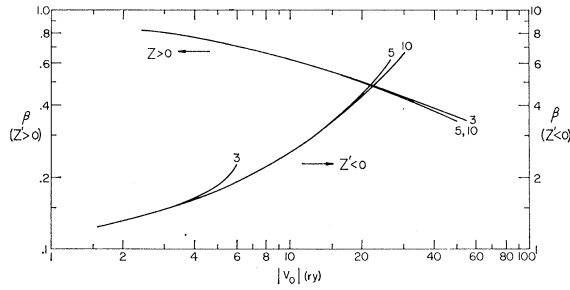


FIG. 1. The computed dependence of $\beta = \alpha/\alpha_1$ [see Eqs. (5) and (6)] on v_0 for positive and negative Z' at several values of ρ_0 .

where $\rho_0 = r_0/\lambda$, and λ is the screening distance, equal to $(\frac{1}{4}\pi)^{1/2} E_{F0}^{-1/4}$. The boundary conditions are now

$$\begin{aligned} dw/dx = w = 0, & \quad \text{at } x = 1 \\ w = v_0 = -2Z'/\lambda E_{F0}, & \quad \text{at } x = 0. \end{aligned} \tag{3b}$$

For various values of ρ_0 , integrations were carried out for a sequence of choices of ϵ , and the value of v_0 was determined in each case. The integrations were carried out by the Runge-Kutta formula⁹ on a grid with $\Delta x = 0.01$. For each choice of ϵ and ρ_0 , a value was determined for $\alpha (= z/Z')$, where

$$z = \frac{4}{3}\pi r_0^3 \delta n(r_0) = (\frac{4}{3}\pi r_0^3) (E_{F0}^{1/2}/3\pi^2) (\epsilon^{3/2} - 1). \tag{4}$$

On combining this with Eq. (3b) for v_0 , one gets

$$\alpha = -(2\rho_0^3/9v_0) (\epsilon^{3/2} - 1). \tag{5}$$

Thus, the set of integrations for a given ρ_0 allows one to calculate α as a function of v_0 . v_0 depends on Z' and E_{F0} , and is therefore determined by the nature of the solvent metal and the charge of the impurity ions. It is convenient to present the results in terms of $\beta = \alpha/\alpha_1$ because it turns out to be independent of ρ_0 , where α_1 , derived by Friedel,¹ is

$$\alpha_1 = \frac{2}{3}\rho_0^2 / (\rho_0 \cosh \rho_0 - \sinh \rho_0). \tag{6}$$

In Fig. 1, we show β plotted against $-v_0$ for several values of ρ_0 for the case where $Z' > 0$. One sees that the curves approach an asymptotic limit which is repre-

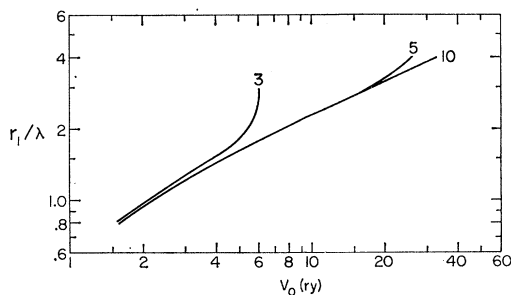


FIG. 2. The normalized distance at which the electron density is zero for negative ions as a function of v_0 , for several values of ρ_0 .

⁹ M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover Publications, Inc., New York, 1965), Sec. 25.5.22.

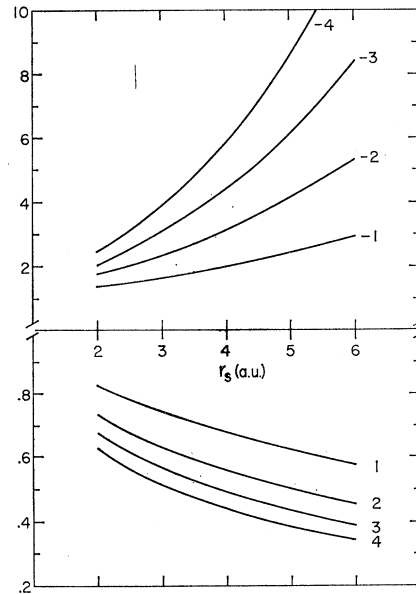


FIG. 3. β versus r_s for various values of Z' .

sented very well by the curve for $\rho_0 = 10$. In metals, $\lambda \lesssim 1 \text{ \AA}$, and the atomic radius is typically 3–5 \AA . Therefore, $\rho_0 = 10$ represents a quite concentrated alloy, and the asymptotic curve is adequate for dilute alloys.

For $Z' < 0$, one must start the integration with $\epsilon < 1$. $v(r)$ will be positive, and increasing with decreasing r . At some value of $r (= r_1)$, δn will become equal to the negative of the original charge density, and further integration is inappropriate (as well as mathematically impossible). Therefore, the value of x at which this occurred in the course of the integration was noted and δn was set equal to its constant limit for smaller values of x . This yielded curves for β versus v_0 plotted in Fig. 1 for several values of ρ_0 . Again, the asymptotic limit is reached fairly well at $\rho_0 = 10$. We also plot in Fig. 2 the values of r_1/λ as a function of v_0 .

For convenience in reference, we show in Fig. 3 curves calculated for β as a function of the spherical radius per electron r_s , in the pure solute, for various values of Z' . Also, the curves for $\rho_0 = 10$ (Fig. 1) have been fitted by a least-squares procedure to an arbitrary function of the form

$$\ln \beta = \sum_{n=1}^4 c_n (\ln |v_0|)^{n-1}. \tag{7}$$

The constants c_n are listed in Table I for the two cases of positive and negative Z' .

TABLE I. Values of coefficients c_n in Eq. 7.

n	Positive Z'	Negative Z'
1	-0.097974	0.13260
2	-0.072060	0.16879
3	-0.035452	0.023361
4	-0.002570	0.022830

The results for copper [calculated by Alfred and March²] and those for silver [by Fujiwara³] agree well with ours for $Z' > 0$. Their calculations were for the limit $\rho_0 \rightarrow \infty$. On the other hand, the calculation by Alfred and March⁴ for $Z' > 0$, which was based on an arbitrary mathematical approximation, is not accurate. Their calculation made use of a determination of the radial distance r_1 , at which the electron density becomes zero. They got 1.66, 2.38, and 2.90 a. u., for $Z' = -1, -2$, and -3 , respectively, which agrees well with our values 1.68, 2.40, and 2.92. However, their corresponding values of β were 1.49, 2.04, and 2.65, as compared to our values 1.66, 2.32, and 3.02.

III. DILUTE METALS

As noted earlier, no background charge is assumed in this case, and we allow for a dielectric constant and effective mass. The basic equations are

$$\nabla^2 V(r) = -8\pi n(r)/K, \quad (8a)$$

$$n(r) = (M^{3/2}/3\pi^2)[E_F - V(r)]^{3/2}, \quad (8b)$$

where K is the dielectric constant and M is the effective-mass ratio. The boundary conditions are

$$V = dV/dr = 0, \quad \text{at } r = r_0 \quad (9a)$$

and

$$dV/dr = 2Z/Kr^2, \quad \text{at } r = r_c \quad (9b)$$

where r_c is the core radius, Z is the total ionic charge of the dilute metal, and $\frac{4}{3}\pi r_0^3$ is the volume per metal atom.

It is now convenient to normalize V by $v = V/E_F$, and to let $x = r/r_0$. Introducing $w = vx$, we have

$$d^2w/dx^2 = -Cx(1-w/x)^{3/2}, \quad (10)$$

where

$$C = (8/3\pi)(M^{3/2}/K)E_F^{1/2}r_0^2. \quad (10')$$

The boundary conditions are

$$w = dw/dx = 0, \quad \text{at } x = 1$$

and

$$xdw/dx - w = -v_0, \quad \text{at } x = x_c \quad (11)$$

where

$$x_c = r_c/r_0$$

and

$$v_0 = -2Z/E_F K r_0. \quad (11')$$

From Eqs. (10') and (11'),

$$-v_0/C = 3Z/E_F^{3/2}r_0^3 M^{3/2}. \quad (12)$$

But the free-electron value of the Fermi energy is

$$E_{F0} = (9\pi Z/4)^{2/3}/M r_0^2. \quad (13)$$

Therefore, the "kinetic-energy-effective-mass" μ_0 is given by

$$\mu_0 = E_{F0}/E_F = (-3v_0/C)^{2/3}. \quad (14)$$

The computations were carried out in a similar manner to those described in Sec. II. For a given set of values of r_0 and r_c , integrations were carried out for a

number of values of C from $x=1$ to $x=x_c$, to determine the corresponding values of v_0 . A single integration procedure was sufficient to determine v_0 for a number of values of x_c (corresponding to the chosen values of r_c) for a given r_0 and C . Then, for each pair of values r_0 and r_c , a curve was calculated for μ_0 versus the "reduced charge" Z_1 , where

$$Z_1 = (M^3/K^3)Z = -9\pi C^2 v_0 / 128 r_0^3. \quad (15)$$

In order to handle the information in a practical way, empirical analytic expressions were computed for μ_0 versus Z_1 by a least-squares method, and the resulting equations were used to calculate μ_0 as a function of r_0 for various values of r_c and of Z_1 . The curves drawn in Fig. 4 are representative of the results obtained.¹⁰ As expected, μ_0 increases rapidly with increasing values of r_0 , and this effect is greater for larger values of Z . The size of the core has an appreciable effect even at large r_0 because most of the screening charge is in the vicinity of the ion. When the dielectric constant is greater than unity, or the effective mass less than unity, the reduced charge Z_1 is smaller than Z , but the nonlinear effect is important at large r_0 even at rather small values of Z_1 . We discuss later the limiting solution for very small Z_1 .

The large values of μ_0 reflect the reduced Fermi energy and smaller density of charge at r_0 in dilute metals. The charge distribution is quite different from the uniform one described by the free-electron model, which provides many of the relations commonly used in an approximate way for metals. A quantity which appears in a fundamental way in many properties of metals is the density of states at the Fermi energy $g(E_F)$. This can be related to the free-electron value by an effective-mass ratio

$$\mu_1 = g(E_F)/g_0(E_F), \quad (16)$$

where the free-electron density of states is given by

$$g_0(E_F) = M^{3/2}E_{F0}^{1/2}/2\pi^2 = (9\pi Z/4)^{1/3}M/2\pi^2 r_0. \quad (17)$$

In terms of the TF model, we obtain $n(E_F)$ by integrating over the volume the value of $g(E)$ at a given r . From Eq. (8),

$$g(E; r)_{E_F} \equiv [dn(r)/dE]_{E_F} = (M^{3/2}/2\pi^2)[E_F - V(r)]^{1/2}, \quad (18)$$

so that the volume integral is

$$g(E_F) = \frac{M^{3/2}}{2\pi^2} \int_{r_c}^{r_0} [E_F - V(r)]^{1/2} \times 4\pi r^2 dr. \quad (19)$$

From Eqs. (14), (17), and (18), one gets an equation in terms of the normalized variables

$$\mu_1 = \mu_0^{-1/2} \times 3 \int_{x_c}^1 (1-w/x)^{1/2} x^2 dx. \quad (20)$$

¹⁰ Because of their lack of physical content, it does not seem worthwhile to reproduce here the large number of constants for these curves. If the reader is interested in having access to these data, they may be obtained by correspondence with the author.

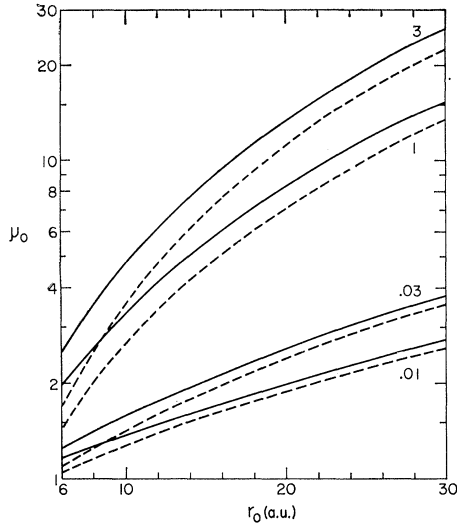


FIG. 4. Dependence of μ_0 on r_0 for various values of Z_1 . The solid curves are for $r_c=1.5$ a. u. and the dashed curves for $r_c=2.1$ a. u.

Calculations for μ_1 were made at the same time as μ_0 , the integral in Eq. (20) being evaluated by means of the Euler-Maclaurin formula.¹¹ The same procedure was used for μ_1 as for μ_0 in deriving its behavior as a function of r_c and Z_1 . Some typical results are shown in Fig. 5.¹⁰

We see that μ_1 decreases below unity as r_0 and μ_0 increase. This is opposite to what one might conclude in terms of free-electron formulas. But it makes sense in terms of what is going on physically in a dilute metal. Since the localized screening charge near the ions grossly reduces the charge density in the large fraction of the volume between the ions, the density of states tends to correspond to a lower electron density in the free-electron model. If one considers the electron density at r_0 , which is smaller than the free-electron value by a factor $\mu_0^{-3/2}$, a free-electron conversion to the density of states $g \sim [n(r_0)]^{1/3}$ predicts that $\mu_1 \sim \mu_0^{-1/2}$. In fact, μ_1 is appreciably larger than that because of the contribution of the higher charge density near the ions.

If the constant C in Eq. (8) is small enough, w/x will be always small compared to unity, and one can linearize the equation to obtain a simple solution:

$$\mu_0^{-3/2} = 1 - x_c^3 + (3/20)Cf_c, \quad (21)$$

and

$$\mu_1 \mu_0^{1/2} = 1 - x_c^3 + Cf_c/20, \quad (22)$$

where

$$f_c = (1 - x_c)^3 (1 + 3x_c + x_c^2). \quad (23)$$

Since the second and third terms are small compared to unity in Eqs. (21) and (22), we get finally

$$\mu_0 = 1 - \frac{2}{3}x_c^3 + Cf_c/10, \quad (24a)$$

and

$$\mu_1 = 1 - \frac{2}{3}x_c^3 + O(C^2). \quad (24b)$$

¹¹ Reference 9, Sec. 25.4.7.

The condition for the linear solution to be valid is that $(\frac{2}{3}C)^{1/2} \ll 1$, which corresponds to $r_0 \ll \lambda$.

The results in Eq. (24) are of little practical interest, because they express merely the small differences of μ_0 and μ_1 from unity in this limit. An interesting aspect of the result is the insight that it provides about the relative roles played by the core volume and the ion potential in μ_0 and μ_1 . The effect of the core exclusion is to decrease both effective masses in proportion to the allowed volume. This agrees with the basic physical idea in the TF approach, which treats the electrons as though their de Broglie wavelength were small compared to r_c . On the other hand, the effect of the potential is to increase μ_0 but not μ_1 , to first order in C . The interesting cases where these two conflicting influences appear strongly are at small r_0 ; i.e., in the range for normal metals not considered in this paper, and occurs, of course, at large C where the nonlinear solution must be used.

The calculation of E_F , and the corresponding μ_0 , is in reference to the potential at $r=r_0$, which is set arbitrarily equal to zero. Only the differences in energies are of significance. The usual way of thinking of the Fermi energy, however, is in reference to the bottom of the valence band. In the present frame of reference, this is best represented by the space-average potential, denoted V_b , so that the Fermi energy with respect to the bottom of the valence band E_{Fb} would be equal to $E_F - V_b$. The effective mass μ_b corresponding to E_{Fb} , equal to E_{F0}/E_{Fb} , would be smaller than μ_0 , since V_b is always negative.

Since a core model is used to reflect the exclusion of the valence-electron wave function from the core region, the space average should also reflect the core exclusion. In other words, we represent the potential of the bottom of the band by the potential energy of a unit charge which is spatially uniform in the region $r_c < r < r_0$. This leads to

$$V_b = \int_{r_c}^{r_0} V(r) \times 4\pi r^2 dr / \frac{4}{3}\pi(r_0^3 - r_c^3) \\ = \frac{3E_F}{1 - x_c^3} \int_{x_c}^1 vx^2 dx. \quad (25)$$

Calculations were made of V_b and μ_b over the same range of variables as μ_1 and μ_0 . It was found that μ_b tended to be equal to the reciprocal of μ_1 ; $\mu_1 \mu_b$ differed from unity usually by less than 10%. This result can be readily understood if one writes μ_0 , μ_1 , and μ_b in terms of the general function

$$\langle (1-v)^n \rangle = 3 \int_{x_c}^1 (1-v)^n x^2 dx. \quad (26)$$

Then one finds that

$$\mu_1 \mu_b = (1 - x_c^3) \frac{\langle (1-v)^{3/2} \rangle^{1/3} \langle (1-v)^{1/2} \rangle}{\langle (1-v) \rangle}. \quad (27)$$

Examination of the ratio containing the bracketed quantities suggests that it should not deviate strongly from unity; and, of course, $1-x_e^3 \sim 1$.

Thus, we see from the behavior of $\mu_1 (\sim \mu_b^{-1})$ and μ_0 in Fig. 5, that the Fermi energy measured from the band edge still is appreciably smaller than the free-electron value at large Z_1 , but the deviation is expressed by a much smaller factor than the value of E_F measured from the potential at r_0 .

IV. DISCUSSION

The results in Sec. II provide in a useable form the correct screening factor for dilute alloys in the TF model which has been used frequently for dilute alloys. However, the exclusion of the valence-electron charge from the core region of the ion, noted in connection with the dilute-metal problem, has significance also for dilute alloys. Omission of this factor causes an overestimate of the screening effect. This overestimate is worse in the nonlinear solution than in the linearized one, because the nonlinear difference occurs mostly at small r . The linear approximation to the mathematical solution also causes an underestimate of the screening, which tends to cancel the opposite error caused by omitting the core region. Therefore, the linear solution may lead to a better result for screening than the nonlinear solution, particularly for positive impurities with a large core radius. It should be noted, on the other hand, that the core error should not be important for $Z' < 0$, since $n(r)$ automatically approaches zero at small r in this case. Therefore, we expect the nonlinear solution to represent screening better for negatively charged impurities, and for impurities with small core size.

It would be desirable to incorporate the core exclusion effect into the dilute alloy solution, not only in the interest of greater accuracy, but also as a mechanism for introducing differences which are known to exist between impurities of the same valence. However, it does not seem possible to do this in a reasonable way in the context of a model where the solute ions are replaced by a uniform positive charge.

The TF results for the dilute metal discussed in Sec. III provide some insight about dilute-metal systems, and some clues about the way in which the concepts based on the free-electron model must be modified. In particular, the gradual development of charge localization and the resulting effect on the Fermi energy and Fermi density of states is elucidated.

It is well known that the usual TF theory does not predict the occurrence of localized states. These will undoubtedly appear at a large enough value of r_0 , probably well within the range of the calculations represented in Figs. 4 and 5. As long as an appreciable fraction of the charge is nonlocalized, however, one may expect that the results of the TF calculation will have some validity.

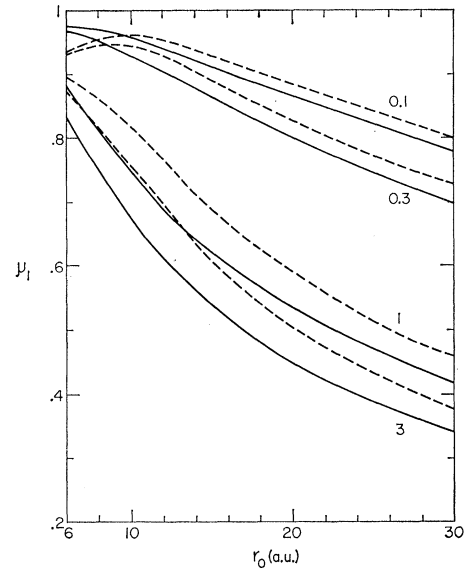


FIG. 5. Dependence of μ_1 on r_0 for various values of Z_1 . The solid curves are for $r_c = 1.5$ a. u. and the dashed curves for $r_c = 2.1$ a. u.

A low-density electron gas would not be stable at ordinary pressures in the absence of a matrix of other atoms. We have allowed for this matrix in a heuristic fashion by means of the dielectric constant K and effective-mass ratio M , whose values might be expected to vary also with r_0 . The reduced charge Z_1 is proportional to $(M/K)^3$, and a decrease in Z_1 causes a decrease in the screening. On the other hand, a decrease in the screening causes the matrix to become more "visible" to the electrons. That is, a larger fraction of the charge will be in the vicinity of the matrix atoms. Therefore, one might look for a rather abrupt change in character of the system, when r_0 is increased beyond the metallic range, and one might expect $(M/K)^3$ to decrease rapidly over a relatively small range of r_0 .

It seems worthwhile to discuss this point in some more detail in spite of the inevitable crudeness in the description. We show in Fig. 6 curves for $n(r)$ for a representative metal with $Z=1$, $M=1$, $K=1$, at several values of r_0 . As expected from the general nature of screening, $n(r)$ falls rapidly with increasing r for large r_0 , and tends asymptotically to the same values for small r . It should be noted that $n > 10^{20} \text{ cm}^{-3}$ at $r < 11$ a. u., or 5.6 \AA , which is about twice the distance between atoms in a typical condensed phase of moderately heavy elements. The electron charge at $r \lesssim 5$ a. u. will overlap the matrix atoms, so that one would expect the charge distribution in such regions to be governed by a dielectric constant greater than unity. We show on the same graph curves for $n(r)$ for the case in which K has a value of 4.62. These curves are higher than for $K=1$ at $r \lesssim 5$ a. u., and lower at smaller r . This is just about the crossover region to neighboring atoms. One would expect the true charge distribution to be represented

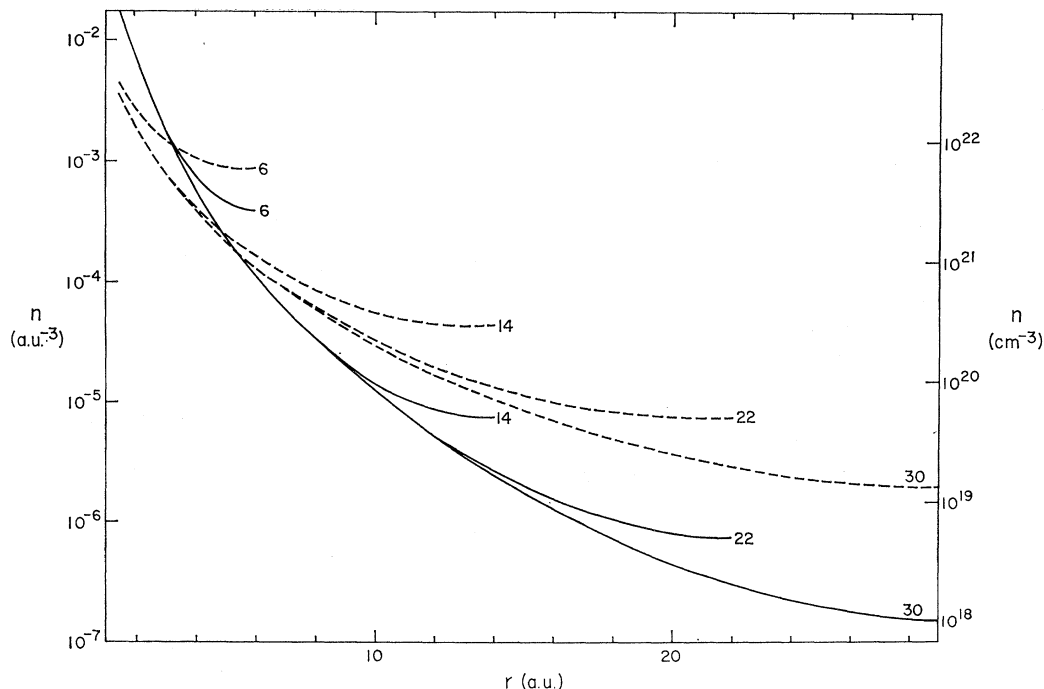


FIG. 6. n versus r for several values of r_0 (in a. u.). These curves were calculated for $r_e = 1.5$ a. u. and $M = 1$, $Z = 1$. The solid curves are for $K = 1$, and the dashed curves for $K = 4.64$.

approximately by a hybrid (renormalized, of course) of the two kinds of curves, reflecting $K = 1$ for $r \lesssim 5$ a. u., and $K > 1$ for $r \gtrsim 5$ a. u. In Fig. 7, the situation is brought out more dramatically by plotting $N(r) = 4\pi r^2 n(r)$. The area under the curve out to a given r [allowing for the log scale for $N(r)$] is the total number of electrons within that distance. One sees that a substantial fraction of the electron charge could be in the matrix region (at $r \lesssim 5$) under the influence of a large dielectric constant, while the rest would be closely tied to the atom at $r \gtrsim 5$ with a distribution like the $K = 1$ curves. If one wished to pursue this idea further, it might be worthwhile to find solutions of the TF equation subject to the assumption that K changes from unity to a larger value at some radius at which the electrons overlap matrix atoms.

This *inhomogeneous* dielectric effect seems likely to occur in dilute metal systems of the type mentioned in the Introduction. This complexity is in addition to the modification of dielectric screening which occurs when a *homogeneous* electron gas is diluted. The description of the latter situation is in itself a complicated problem, and the theory is not very clear at present. Theoretical studies suggest, however, that between the extremes of a concentrated homogeneous gas, with $r_0 < 6$, and a dilute one, the dielectric constant changes from unity to a constant final value, and the final situation would be describable by an effective mass reflecting the density

of states at the bottom of the valence band.¹² The results in this paper seem consistent with this with the following modification: When the positive charge is discrete as it is in a real system, instead of diffuse as in the homogeneous electron gas, a large fraction charge associated with each metal atom remains in the immediate vicinity of the atom, and the density of the electron charge in most of the volume is correspondingly reduced.

As explained above, one would expect a rather abrupt change in screening character as r_0 is increased. This would probably occur in the range where the metal atoms have densities of 10–50% of the normal metallic density. This change is akin to a phase transition, and indeed, the energetics of the system may well lead to a separation into two phases, one metallic ($r_0 < 6$) and the other semimetallic ($r_0 \gg 6$). Such phase instabilities have been observed in a number of dilute-metal systems, and have been discussed in connection with the Mott transition.¹³ The present discussion indicates that the second (nonmetal) phase need not be an insulator. Indeed, the general implication of the TF treatment is that partial localization of electron charge occurs when metal atoms

¹² D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), Chap. 3.

¹³ D. E. Bowen, J. C. Thompson, and W. E. Millett, *Phys. Rev.* **168**, 114 (1968). See also papers and discussions presented at the International Conference on the Metal-Nonmetal Transition [*Rev. Mod. Phys.* **40**, 673 (1968)] and particularly those papers by N. F. Mott (p. 677), J. C. Thompson (p. 704), and M. H. Cohen (p. 839), and the comment by M. Cutler at the end of Thompson's paper (p. 709).

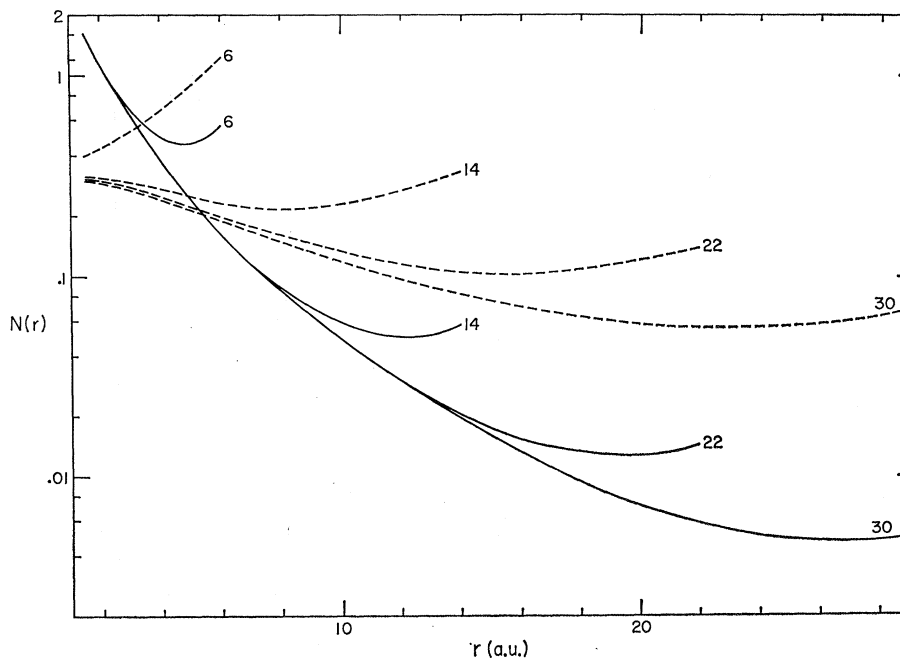


FIG. 7. $4\pi r^2 n$ versus r for several values of r_0 (in a. u.) These curves were calculated for $r_0 = 1.5$ a. u. and $M = 1$, $Z = 1$. The solid curves are for $K = 1$, and the dashed curves are for $K = 4.64$.

are diluted, so that the dilute metal, particularly one with a dielectric matrix, may not differ greatly in energy from an insulator.

Finally, some remarks should be made with regard to a discussion of screening which was presented in Ref. 5. In that work, a comparison of experimental results with conventional theory for the behavior of the thermoelectric transport parameters of n -type thallium-tellurium liquid alloys showed very good agreement except for the fact that the deduced value of the de Broglie wavelength λ_d of the electrons was too small in comparison with the scattering distance λ_s . This is inconsistent with the original assumptions of the theory. It was observed that if a nearly constant fraction α_c of the electrons is assumed not to participate in the transport, this would increase the ratio of λ_s to λ_d , and the discrepancy would be removed. A study of nonlinear TF screening, which constituted an early phase of the present work, seemed to support this idea. That conclusion was based on the assumption that the effective electron density was represented by $n(r_0)$, and that the electrons otherwise had properties given by free-electron theory. In these terms, one has a free-electron band with a fraction α_c of the total valence-electron density, where $\alpha_c = \mu_0^{-3/2}$. Considerations presented in this paper suggest that such a point of view is too crude. For instance, the density-of-states effective mass μ_1 is appreciably larger than $\mu_0^{-1/2}$.

However, the results in this paper do seem to provide some support for an effective charge model. The intuitive basis for this model lies in the fact that a fraction of the valence-electron charge is closely tied to the ions, while the remainder (in the dielectric matrix) is rela-

tively diffuse and more nearly uniform in density. It seems reasonable to expect that an applied electric field or other force would cause a large flux in the diffuse charge as compared to that in the closely bound charge. Of course, this idea ascribes different dynamic properties to two parts of the charge distribution, a point of view which does not seem to receive support from existing theoretical treatments of transport. In essence, we are suggesting that some of the localized charge can act like it is fully bound without necessarily being in discrete energy levels.

It is interesting to make comparison with the partial-wave scattering theory in dilute alloys. The partially localized charge in that case is identified with the phase shifts of the outgoing waves through the Friedel sum rule.¹ However, the contribution of the impurity atom to the resistivity is arrived at from the phase shifts through a consideration of interference between ingoing and outgoing waves, which leads to a reduction of the mobility. This kind of theory does not yet seem to have been extended successfully to concentrated alloys or dilute metals. But it seems possible that when the scattering rate is large enough compared to the bandwidth (in appropriate units), the result may be one better described in terms of complete immobilization of part of the localized charge.

The relationship of the various effective masses, deduced in this paper from the TF model, to the corresponding parameters used in transport theory is not clear. But they do suggest a picture of a band containing a fraction α_c of the valence electrons which has roughly the relationships of a free-electron band. The free-electron relationships would suggest that α_c would be related

to the density-of-states effective mass by $\mu_1 = \alpha_c^{1/3}$ and to the bandwidth effective mass by $\mu_b = \alpha_c^{-2/3}$. Thus, one would expect $\mu_1^2 \mu_b \cong 1$. Instead, we observe that $\mu_1 \mu_b \cong 1$, or $\mu_1^2 \mu_b \cong \mu_1$. In Ref. 5, it was found that α_c in Tl-Te might be as large as 0.5. This leads to $\mu_1 \cong 0.8$, which is not too far from unity. In this range then ($\alpha_c \gtrsim 0.5$), the TF model yields parameters roughly

consistent with a free-electron band with a reduced electron density.

ACKNOWLEDGMENT

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Phonon Scattering by Conduction Electrons and by Lattice Vacancies in Carbides of the Transition Metals*

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The scattering of phonons by point defects in high concentrations and by electrons has been studied in the cubic transition metal carbides. The specimens were single crystals containing up to 24% carbon-atom vacancies: TiC_x , ZrC_x , and NbC_x , with $0.76 \leq x \leq 0.96$. Although the lattice thermal conductivity K_l is indeed low in these materials at low temperatures, the data and a Callaway analysis show that the observed suppression of K_l cannot be explained solely by Rayleigh scattering from point defects. Furthermore, the dependence of K_l on vacancy concentration is weak and of the wrong sense. A good fit to the data is obtained by introducing an additional term in the inverse relaxation time proportional to ω^2 . Pippard has shown that such a term represents phonon scattering by conduction electrons if the concentration of conduction electrons n is sufficiently high, and the electron mean free path λ_e is less than the dominant phonon wavelength. For the carbides, these conditions are met: $n \sim 10^{21}/\text{cm}^3$, and λ_e is only a few lattice constants even at low temperatures, because of the scattering of electrons by lattice vacancies. We conclude that at low temperatures K_l for the carbides is dominated by the scattering of phonons by conduction electrons. However, point defects influence the thermal conductivity of these solids both directly by scattering phonons and electrons and indirectly by altering the phonon-electron interaction.

I. INTRODUCTION

THE measurement and analysis of thermal conductivity K has proved to be a powerful technique for studying defects in crystalline solids.¹ The technique is particularly effective at low temperatures. In this temperature region, the lattice thermal conductivity is primarily controlled by crystal defects, boundary scattering, and umklapp scattering. Since these various types of processes influence the temperature dependence of K in different ways, the technique permits the identification of the defect present in a given specimen and a determination of its concentration.

Analysis of a complex system containing several varieties of defects—dislocations, stacking faults, grain boundaries, point defects, conduction electrons, etc.—was made feasible by the advent of the Callaway formalism.² In this analysis, the individual inverse

relaxation times for the various phonon scattering processes are summed to give a net inverse relaxation time which is frequency-dependent. This quantity is then substituted into a Debye-like integral which is evaluated numerically to give the total thermal conductivity.

A challenge to the adequacy of the above technique is provided by the transition-metal carbides, an interesting class of hard, semimetallic, high-melting temperature compounds.³ These materials contain high concentrations of point defects (carbon-atom vacancies) and conduction electrons, plus some grown-in dislocations and sub-boundaries. Carbon-atom vacancies have been found to be strong electron-scattering centers for electrical conduction in TiC,⁴ and previous high-temperature measurements^{5,6} have shown some unexpected behavior of the lattice conductivity. We here test the suggestion⁷ that the *thermal* conduction behavior is also defect controlled.

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¹ For a review of the subject, see P. G. Klemens, *Solid State Phys.* **7**, 1 (1958).

² J. Callaway, *Phys. Rev.* **113**, 1046 (1959).

³ See, for example, W. S. Williams, *Science* **152**, 34 (1966).

⁴ W. S. Williams, *Phys. Rev.* **135**, A505 (1964).

⁵ R. E. Taylor, *J. Am. Ceram. Soc.* **44**, 525 (1961).

⁶ R. E. Taylor, *J. Am. Ceram. Soc.* **45**, 353 (1962).

⁷ W. S. Williams, *J. Am. Ceram. Soc.* **49**, 156 (1966).