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Electroreflectance of highly conducting materials by deep field penetration*

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We report the results of an investigation into a new technique to obtain band-structure-specific electroreflectance data from highly conducting materials. The basis for the work is that an electric field can penetrate into a thin conducting film, if the total number of carriers available for terminating the field is less than the number of carriers producing the field. A semiclassical theory is developed to calculate the field profiles. The role of free carriers in producing a field-induced change in reflectance and the various models for predicting the response are examined. The choice of experimental approach and the areas of applicability of the technique are discussed. It appears feasible to use this technique for band-structure investigations of materials with free-carrier densities up to about 10^{20} cm^{-3}.

I. INTRODUCTION

Among the various branches of modulation spectroscopy, electroreflectance (ER) is a powerful diagnostic tool for the exploration of the band structure of semiconductors and dielectrics. Since the line shapes are related to the third derivative of the unperturbed dielectric function, ER enhances the critical-point structure and suppresses the noncritical background more effectively than first-derivative techniques such as piezo- or thermoreflectance. Because the vectorial character of the modulating electric field lowers the symmetry of the material under study, anisotropies of considerable symmetry-analytical value result.

In view of its impact on the formulation of accurate band models of nonconducting media, it is unfortunate that problems of free-carrier effects prevented equally diagnostic results from being obtained in highly conducting materials. In spite of the precise knowledge of the Fermi surface derived from magnetic-resonance data, there is a need for experimental information on the band structure *away* from the Fermi energy. A better test of band-structure calculations requires experimental information over a much wider energy range, such as that provided by ER data.

Unfortunately ER data for metals representative of the bulk properties are not available. In a metal the modulating field is screened out by free carriers within the Thomas-Fermi screening length of less than 1 Å, leaving a field-free region over most of the penetration depth of the light.

ER spectra have been observed at metal-electrolyte interfaces for a number of metals. The first report by Feinleib[1] indicated that the spectra are closely related to structure in the static reflectance curve of the metals. A number of studies followed that were characterized by an increasing sophistication in experimental control[2,3] and theoretical interpretation.[4-9] Although the various authors present differing models for interpreting the modulated spectra, they agree that external modulation of the free-carrier effects in a thin-surface region is the source of the reflectance change.

The free-electron part of the dielectric function is only loosely connected to the band structure. Modulation of the plasma frequency and the band population are the principal free-carrier effects in conductors as opposed to the modulation of the combined density of states, the main mechanism of ER in nonconducting materials. This paper investigates the conditions under which the free-carrier screening at the surface can be reduced to permit observation of the modulation of the band structure of the bulk material.

In Sec. II the field-induced changes in the dielectric function arising from perturbation of the band structure and free-carrier density are discussed. Previous approaches to the theoretical description of the ER of metals are reviewed: various models, their success in interpreting the data, and their relationship to each other are described.

In Sec. III a technique for obtaining bulk related ER data from conducting materials is presented. It is based on the hypothesis that a static electric field can penetrate a thin conducting film if the number of surface charges producing the field is comparable to or greater than the total number of charges contained in the film. The conditions necessary for deep field penetration in a conductor and a semiclassical theory to predict the resultant field profiles are discussed, including numerical solutions and limitations of the theory. The experimental requirements and the materials in which the experimental technique is applicable are discussed.

II. FUNDAMENTAL MECHANISMS OF ELECTROMODULATION

It is important to clearly distinguish between the contributions to the field-induced change in reflectivity that arise from the perturbation of the band structure, and that are due to the presence of free carriers, since they lead to quite different information about the solid. The density of the free carriers is the parameter that determines which mechanism will dominate. In general, the ER results in semiconductors show sharper structure, while the response from electrolytic measurements on metals is much larger. All the ER experiments, except possibly some work on metals, have had as their goal the determination of the band-structure parameters. In the following discussion we examine the circumstances under which this goal can be achieved.

We first examine the fundamental mechanisms by which an applied electric field can change the dielectric function. Then the theories relating the change in the dielectric function to the change in reflectivity for various classes of materials are described. Finally, we review the various interpretations of the electromodulation results for metals, and point out the significance of free-carrier effects in a broader class of materials.

A. Field-induced changes in the dielectric function

The optical properties of a crystal are determined by its dielectric function $\epsilon(\omega)$.[10] It can be divided into an intraband part ϵ_{intra} and an interband part ϵ_{inter}. The intraband part is related to the plasma frequency ω_P and the relaxation time τ of the free-carrier gas by means of the relation

$$\epsilon_{\text{intra}} = 1 - \omega_P^2/\omega(\omega + i/\tau) . \qquad (1)$$

The imaginary part of ϵ_{inter} is given by the approximate expression

$$\text{Im}\,\epsilon_{\text{inter}} = \frac{2\pi^2 e^2}{m\omega} P_{12}(\omega)[f_1(k_\omega) - f_2(k_\omega)]\,\rho_{21}(\omega) . \qquad (2)$$

Here $P_{12}(\omega)$ is the effective oscillator strength for the optical transition from the initial band 1 to the final band 2 at photon energy $\hbar\omega$; f_1 and f_2 are the distribution functions for bands 1 and 2, respectively; k_ω is the solution of the energy-conservation equation $E_2(k_\omega) - E_1(k_\omega) = \hbar\omega$; and $\rho_{21}(\omega)$ is the combined density of states. The real part of ϵ_{inter} may be related to the imaginary part by means of the Kramers-Kronig transformation.

If there are no free carriers ($f_1 = 1$, $f_2 = 0$) the field influence on the dielectric function reduces to that of the combined density of states and the oscillator strength.[11] These effects are particularly large at critical points of the interband energy. The most pronounced changes are caused by the Franz-Keldysh effect.[12] In typical cases the order of magnitude of the relative field-induced change of ϵ due to the Franz-Keldysh effect is 10^{-2} at field strengths of 10^4 V/cm.

When a static electric field is applied *in the presence of free carriers,* and no electric current is allowed to flow, an accumulation or depletion layer is established in the surface region that is being probed by light. This modification in the free-carrier density can produce a change in the dielectric constant in two ways. (There is also a dependence of the band structure and the relaxation time on the carrier density, which can result in an additional free-carrier-induced field effect of the dielectric function. The latter effect has not been investigated in detail. It is probably small and will be omitted in the further discussion.) First the Fermi energy shifts, causing a change in the band population,[13] and second, the plasma frequency is changed.

The change in the interband part of the dielectric function due to the change in the band population is given by

$$\Delta\epsilon_{\text{inter}}^{(\text{BP})} = \frac{\Delta f_1(k_\omega) - \Delta f_2(k_\omega)}{f_1(k_\omega) - f_2(k_\omega)}\,\epsilon_{\text{inter}} ,$$

where

$$\Delta f_i(k) = (\Delta n/n)(E_{B_i}/\kappa T)^{3/2} e^{-E_i(k)/\kappa T}$$

for a classical gas, and

$$\Delta f_i(k) = (\exp\{[E_i(k) - E_{F_i}(n + \Delta n)]/\kappa T\} + 1)^{-1}$$
$$-(\exp\{[E_i(k) - E_{F_i}(n)]/\kappa T\} + 1)^{-})^{-1}$$

for a quantum gas. The quantities in the above expressions are given by

$$E_{B_i} = (\hbar^2/2m_1^*)\ (2^{2/3}\sqrt{\pi}/a)^2,$$
$$E_{F_i}(n) = \tfrac{3}{2}(2\pi)^{-1/3}E_{B_i}(n/N)^{2/3} ,$$
$$E_i(k) = (\hbar^2/2m_i^*)k^2.$$

m_i^* is the effective mass of the carriers in band i, N is the number of unit cells per cm^3, and the subscripts B_i and F_i refer to a Boltzmann and Fermi gas, respectively. The value of Δn for an electric field E_0 screening distance d, and static dielectric constant of the core of the atoms ϵ_0, is given by

$$\Delta n = \epsilon_0 E_0 / 4\pi d \ .$$

This formula applies for low values of depletion and all values of accumulation. The magnitude of $\Delta\epsilon^{(\mathrm{BP})}_{\mathrm{inter}}$ and its dominance of the band-structure related change in $\Delta\epsilon^{\mathrm{FK}}_{\mathrm{inter}}$ depends on n, Δn, the photon energy, temperature, and effective masses. In the case of a quantum gas $\Delta\epsilon^{(\mathrm{BP})}_{\mathrm{inter}}$ is particularly large for optical transitions that have initial or final states near the Fermi energy. It has a nearly exponential decrease for higher photon energies because of the $f_i(k_\omega)$ dependence. For a classical gas and a direct gap semiconductor at the fundamental threshold, $\Delta\epsilon^{(\mathrm{BP})}_{\mathrm{inter}}$ becomes of the same order of magnitude as $\Delta\epsilon^{(\mathrm{FK})}_{\mathrm{inter}}$ when the carrier density reaches $\simeq 10^{17}$ cm^{-3} and it dominates for higher densities. These conclusions hold for field values of 10^4 V/cm, $m_1^* = m_2^* = m$, and room temperature.

The change in the intraband part of ϵ due to the change of the plasma frequency is given by $\Delta\epsilon_{\mathrm{intra}} = (\Delta n/n)(\epsilon_{\mathrm{intra}} - 1)$. The fractional change $\Delta n/n$ may be near unity for the whole range of carrier concentrations for sufficiently high fields. This is particularly true for metals if the surface field strength is $E \gtrsim 10^7$ V/cm. In this case $\epsilon_{\mathrm{intra}}$ can contribute substantially to the total change of the dielectric function provided that $\epsilon_{\mathrm{intra}}$ itself does not approach unity (as is the case for lower carrier densities). At metallic densities and optical frequencies, the quantity $\epsilon_{\mathrm{intra}} - 1$ is of the same order as $\epsilon_{\mathrm{inter}}$, and $\Delta\epsilon_{\mathrm{intra}}$ becomes comparable to ϵ itself. Therefore at high carrier densities (metals) and extremely high electric fields ($E_0 \gtrsim 10^7$ V/cm), both of the free-carrier mechanisms can produce relative changes of the dielectric function of the order of 1, rather than 10^{-1}, the characteristic value for the Franz-Keldysh effect at the same field strength. However, the field penetration is restricted to the first atomic layers of the sample.

Strictly speaking the comments in the above paragraph are correct only if the electric field is spatially homogeneous. They are approximately true if the field penetration depth d is large compared to the characteristic wavelength of the optically responding charge carriers. In that case the field homogeneity can be treated by replacing the constant field by a spatially varying field in an expression for $\Delta\epsilon$ that has been obtained from the homogeneous case. In metals, the field penetration depth may be comparable to the wavelength of the optically responding electrons. When this occurs the field inhomogeneity must be taken into account expressly in calculating the electron states in the surface region. The concept of a surface dielectric polarization may be more natural in this case than that of a bulk polarization.

B. Electroreflectance in various classes of materials

The following discussion deals with the various phenomenological theories that relate the change in the dielectric function $\Delta\epsilon$ to the reflectivity change ΔR. In insulators and semiconductors with few free carriers, the change in reflectivity is determined mainly by the perturbation of the combined density of states. The screening length is much greater than the characteristic absorption length for photons in the band transition region, so that the field may be considered to be spatially homogeneous and the change in reflectivity may be calculated using Fresnel's formula. In nondegenerate semiconductors with higher carrier densities, the microscopic mechanisms responsible for the electroreflectance response again resides in the change of the combined density of states, but the electric field can no longer be considered constant over the light penetration depth. In this case, the reflectivity change can be calculated by the use of the Eikonal approximation[14] if the condition

$$|\Delta\epsilon/\epsilon| \ll d\,|q| \tag{3}$$

is fulfilled where d is the screening and q is the complex wave number of the light given by $q = (\omega/c)(n + ik)$. If so, the Fresnel formula may be used to calculate the reflectivity change using a weighted spatial average of $\Delta\epsilon$.[14]

In highly doped semiconductors and semimetals, free carriers affect the electric-field-induced change in ϵ, and limit the field penetration distance. As a consequence, the conditions for the application of the Eikonal approximation are violated. For example, consider a material containing a degenerate electron gas with a density of 10^{20} cm^{-3}. The Thomas-Fermi screening distance is only 1.7 Å. In the interband transition region, the absorption coefficient typically reaches values of $K = 4$, giving light penetration depths on the order of 100 Å. Then a field-induced change of ϵ of 10^{-2} is too large for the Eikonal approximation to apply.

In metals, the change of the dielectric function is restricted to such a small sample region it can only give rise to measurable changes in reflectivity if the change is relatively large. Such changes in ϵ are produced by free-carrier effects, but not by the electric field influence on the band structure. There are several approaches to the problem of calculating the reflectivity change in terms of the dielectric function.

C. Review of previous interpretations

McIntyre[7] has reviewed the earlier attempts of Feinleib,[1] Stedman,[5,6] Prostack and Hansen[4] and showed that they do not adequately provide a basis for the interpretation of the experimental results in metals. The same paper contains an approach proposed by McIntyre and Aspnes[8,15] to explain the ER data. A three-component medium is considered that consists of the metal, the electrolyte, and an intermediate layer that has a thickness small compared to the wavelength of the light. The intermediate layer is defined by the region at the metal-electrolyte interface characterized by a strong perturbation of the dielectric function. One of the possible assumptions—the only one of interest in this context—is to identify the intermediate layer with the space charge region of the metal. The change of the dielectric function in this region is attributed to the change of the plasma frequency. The related change of reflectivity is calculated by means of a linear expansion[7] with respect to the small parameter d/λ. McIntyre obtains favorable comparisons with his experimental results[2,7] in the case of gold, but much poorer agreement for copper. Another model involving an intermediate layer was recently proposed by Howson *et al.*[16] However, the agreement with experiment is even less convincing and we will not discuss the results in further detail.

A different approach is offered by Garrigos,[17] Garrigos *et al.*[9] and Cheyssac *et al.*[18] In this model, the boundary-value problem is explicitly modified to include the presence of surface polarization current due to the additional charge carriers brought to the surface by the electric field. This current enters in the relationship for matching the values of the tangential component of the magnetic field vector of the incident light wave at the boundary as

$$\hat{n}\times(\vec{H}_1-\vec{H}_2)=\xi\vec{E}_t, \tag{4}$$

where $\hat{n}$ is the normal facing away from the metal, $\vec{H}_1$ and $\vec{H}_2$ refer to the magnetic fields of the light wave in the incident medium and metal, respectively, $\vec{E}_t$ is the tangential electric field of the light wave in the metal, and ξ is the surface conductivity in the metal due to the presence of the static surface field. The term ξ vanishes for zero excess charge, and Eq. (4) reduces to the usual uncharged electromagnetic boundary-value condition.

Garrigos[17] then calculates the modified Fresnel formula for an electromagnetic wave reflected from a plane surface. By assuming a complex frequency-dependent surface conductivity Garrigos obtains excellent agreement with the experimental values of $\Delta R/R$ for a wide range of angles of incidence for gold, copper, and silver. The agreement is substantially better than that obtained by McIntyre for Howson *et al.* and argues for the applicability of the surface-current approach.

The excess surface-current density ξ may not be isotropic, even in cubic materials, since the crystal is distorted by the presence of an electric field.[19] Thus, it is possible to observe polarization effects in ER due to such anisotropic currents. Recently Furtak and Lynch[3] reported polarization-dependent ER in Ag and interpretated their results in terms of a band-structure perturbation. An alternative explanation is given by the presence of such an anisotropic surface current.

All of the above approaches are equivalent in that they consider a thin intermediate layer between the sample and its surroundings where the change in reflectivity occurs. In the McIntyre-Aspnes approach the thickness of the layer is small compared to the wavelength, but not zero. There is no obvious way to choose the dielectric function of this layer. On the other hand, Garrigos[17] assumes an intermediate layer of zero thickness, but with finite surface conductivity. The free parameter in this approach is the surface conductivity. It is easier to make a reasonable assumption about the surface conductivity rather than about the dielectric function of an interior phase with a finite extension. This simplicity, coupled with the excellent experimental agreement, favors the later approach for the interpretation of the electroreflectance of metals. Additionally, the surface current approach may have a much wider application than to metals alone. The condition $d|q|\ll 1$ is met for semimetals and some highly doped semiconductors in the band transition region. Thus, the interpretation of electroreflectance spectra from these materials may bear reexamination in terms of this model.

In view of the above discussion, it might be concluded that electroreflectivity as a band-structure probe, in its usual form, is not useful in metals because it is dominated by free-carrier effects. However, if the Thomas-Fermi screening mechanism could be modified to produce substantial field penetrations, information about the critical points in the band structure might be retrieved. That is precisely what our approach is designed to accomplish.

III. FIELD PENETRATION

The penetration of static electric fields into conducting materials is limited by the shielding effect of free charge carriers provided the current density is zero. The exact theoretical field profile depends on the extent to which the various quantum, many body, and surface effects are taken into account.[20-23] A rough estimation of the field penetration can be obtained by means of the linearized Debye or Thomas-Fermi approximation for a classical or Fermi gas, respectively. According to these approximations, the field decreases exponentially within the sample with a characteristic decay length equal to the Debye or Thomas-Fermi screening length. The corrections that may result from a more rigorous theoretical treatment do not drastically alter the depth over which the electric field is remarkably different from zero.

The question arises: are there any possible conditions for which the penetration of an external electric field into a metal can be made much stronger than in the case of exponential screening? The answer is very simple. Exponential screening in the case of an electrically neutral sample applies only if the total number of free carriers within the sample is large compared to the number of external charge carriers used to create the electric field. If, however, the number of external carriers is comparable with, or larger than, the total number of free carriers within the sample, the screening breaks down and the field lines penetrate. This situation may be achieved by making the external field high enough and by using a sufficiently thin and properly insulated sample. To give an example: A metal film of 100 Å thickness and a surface of 1 cm^2 contains about 10^{15}–10^{16} free carriers. The number of charge carriers on 1 cm^2 of a totally polarized ferroelectric can reach 2×10^{14}. From this we conclude that the concept of a limitation of the screening capability of free carriers might be of interest even in the most striking case of real metals.

If the sample is not insulated but grounded, charge will flow to or from the sample on the application of an electric field. For negative electrode polarity, electrons flow out of the sample and the charge flow is limited to the total number of free electrons within the sample. If the polarity is positive, electrons flow into the sample from the ground. In this case, the usual screening takes place.

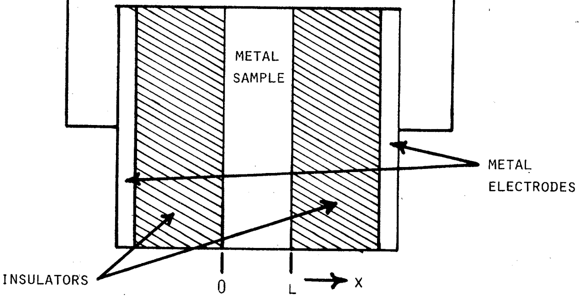

FIG. 1. Field production in an isolated metal sample.

The purpose of this section is to give a simple theoretical formulation of the concept of charge-limited screening. Our theoretical treatment is based on the quasiclassical description of the electron gas, with the assumption of approximate local thermodynamic equilibrium. We consider a metal plate of thickness L surrounded by an insulating medium. The static electric field is applied in the direction of x normal to the sample by applying a dc voltage to the insulator surfaces (Fig. 1). The sample consists of fixed positive charge carriers of density ρ_0, and free negative carriers. The negative charge density $\rho(x)$ is a function of position x within the sample. It is assumed that the sample is electrically neutral, i.e.,

$$\int_0^L dx[\rho_0 - \rho(x)] = 0 \ , \tag{5}$$

and the current density $\vec{j}$ within the sample is zero. Further we assume that the total number of free carriers in the sample cannot change under an applied field. These three assumptions may be violated in real cases. A qualitative discussion of the related effects is given at the end of this section.

The electric field value $E(x)$ is connected with the total charge density $\rho_0 - \rho(x)$ by Poisson's equation,

$$\frac{dE}{dx} = \frac{4\pi}{\epsilon_0}\,[\rho_0 - \rho(x)] \ . \tag{6}$$

The electric field and density gradient result in electric currents that cancel under our conditions. If the perturbation of the *local* equilibrium is not too strong, the currents are linear in the driving forces and we have the equation,

$$0 = \mu\rho(x)E(x) + D\,\frac{d\rho}{dx} \ . \tag{7}$$

Here $-\mu$ is the mobility of free carriers, and D their diffusion constant.

The electron gas is far from *total* thermodynamic equilibrium under these circumstances, so that μ and D depend on the local value of the chemical potential. The electron temperature is not dependent on position and is equal to the lattice temperature.[24] The charge density and field strength can be calculated from Eqs. (6) and (7). To make the solution unique, boundary conditions have to be added. When Poisson's equation is combined with the neutrality condition (5) we obtain the first boundary condition,

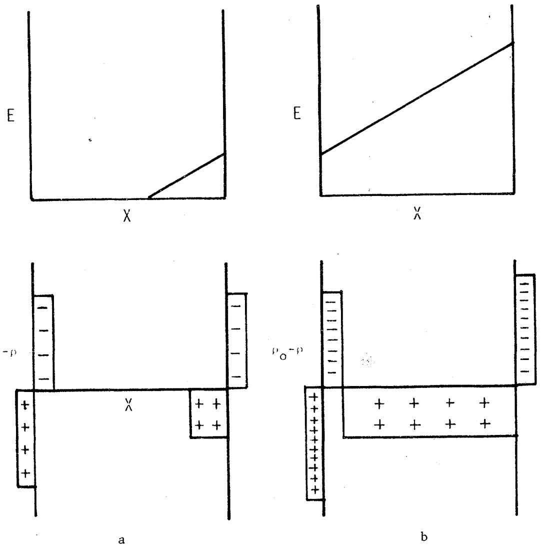

FIG. 2. Field and charge profiles in an isolated thin film neglecting diffusion: (a) $\sigma < \rho_0 L$, (b) $\sigma > \rho_0 L$.

$$E(0)=E(L)\ . \tag{8}$$

As the second condition, we fix the electric field strength at the surface to be E_0:

$$E(0)=E_0\ . \tag{9}$$

The surface field value E_0 is connected with the external surface charge density σ by a relation $E_0=4\pi\sigma/\epsilon$.

In order to illustrate the character of the solution we first solve the problem neglecting the diffusion. Without the diffusion current it follows from Eq. (7) that

$$\begin{aligned} &\rho(x)=0, \quad \text{where } E(x)\neq 0 \\ &E(x)=0, \quad \text{where } \rho(x)\neq 0\ . \end{aligned} \tag{10}$$

If the number of external surface charges is less than the total number of free carriers within the sample, i.e., $\sigma<\rho_0 L$, the sample splits into two regions separated at $x=x_0\equiv L-\sigma/\rho_0$ with the electric field strength given by

$$E(x)=\begin{cases} 0 & \text{for } 0\leq x<x_0, \\ (4\pi/\epsilon)(x-x_0)\rho_0 & \text{for } x_0\leq x\leq L. \end{cases} \tag{11}$$

The field and charge solutions for this case are diagramed in Fig. 2(a). When the number of external charges is greater than the number of free carriers in the sample or $\sigma\geq\rho_0 L$, there is no field-free region within the sample and therefore, no region with free carriers. All free carriers are located on the $x=0$ surface of the sample. Then the electric field $E(x)$ is given by

$$E(x)=(4\pi/\epsilon)(\sigma-\rho_0 L)+(4\pi/\epsilon)\rho_0 x\ . \tag{12}$$

and is diagramed in Fig. 2(b).

In the grounded case, the field strength is zero within the sample for positive polarity, but for negative polarity two cases may be distinguished depending upon the length $x_1=\sigma/\rho_0$. If $x_1\leq L$, then ($\sigma\leq\rho_0 L$) $E(x)$ is analogous to Eq. (11), except that ϵ_0 is the appropriate dielectric constant. On the other hand if $x_1\geq L$, $E(x)=-(4\pi/\epsilon_0)(\sigma-\rho_0 x)$, and the field penetrates through the film.

It is obvious that the inclusion of the diffusion term will not completely alter the field and charge distributions, but will only smooth them out. If diffusion is included, we obtain from Eqs. (6) and (7) the equation,

$$\frac{d^2E}{dx^2}+\frac{\mu}{D}E\frac{dE}{dx}-\frac{4\pi}{\epsilon_0}\frac{\mu}{D}\rho_0 E=0\ . \tag{13}$$

Using Einstein's relation $\mu/D=e/\kappa T$, for a classical gas, the expression $[(\epsilon_0/4\pi\rho_0)D/\mu]^{1/2}$ becomes the Debye screening length $d=[\epsilon kT/4\pi e\rho_0]^{1/2}$. For a Fermi gas the ratio μ/D is equal to $2e/3E_F$.

The Fermi energy is not constant, but varies with x according to $E_F(x)\simeq[\rho(x)]^{2/3}$. The expression $[(\epsilon_0/4\pi\rho_0)D/\mu]^{1/2}$ becomes equal to $[\rho(x)/\rho_0]^{1/3}d$, with $d=[\epsilon_0 E_F/6\pi e\rho_0]^{1/2}$ as the Thomas-Fermi screening length under equilibrium conditions. It is useful to introduce the sample thickness L as the natural unit of length, and the surface field strength E_0 as the natural unit of field strength: $x=\hat{x}L$, $\hat{E}(\hat{x})=\hat{E}(\hat{x})E_0$. With the normalized quantities $\hat{x}$ and $\hat{E}$ Eq. (13) becomes

$$\frac{d^2\hat{E}}{d\hat{x}^2}-\alpha^2\hat{E}\left(1-\beta\frac{d\hat{E}}{d\hat{x}}\right)^{\gamma}=0, \tag{14}$$

where $\alpha=L/d$ is the sample thickness in units of d, $\beta=\sigma/\rho_0 L$ the ratio of the number of external surface charge carriers to the total number of free carriers within the sample $\gamma=1$, or $\frac{1}{3}$ for the classical or Fermi gas, respectively. Equation (14) may also be obtained in a slightly different way. By differentiating Poisson's equation with respect to x and using the local Boltzmann or Fermi distribution for $\rho(x)$, one immediately obtains Eq. (14)—including the nonlinear term proportional to β that is usually omitted.

If the number of external surface charge carriers is small compared to the total number of free carriers within the sample, i.e., $\beta\ll 1$, the nonlinear term in Eq. (14) can be neglected. Then the field is given by

$$\hat{E}(\hat{x})=\frac{\cosh(\frac{1}{2}-\hat{x})/\alpha}{\cosh(1/2\alpha)}\ . \tag{15}$$

The electric field strength drops off approximately exponentially away from the boundaries at $\hat{x}=0$ and $\hat{x}=1$ and the characteristic length of the decrease given by the screening length d. When the

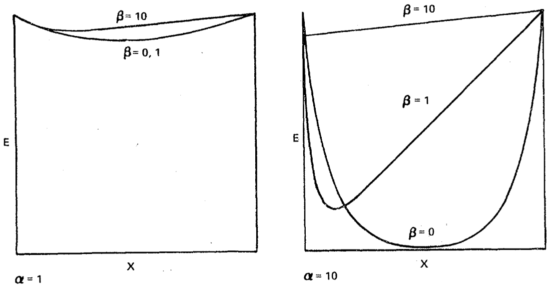

FIG. 3. Field profiles for various values of α and β for a classical electron gas.

number of external surface carriers is comparable to or larger than the total number of carriers of the sample, the exponential screening no longer holds. If in that case the screening length d becomes small compared to the sample thickness, $1/\alpha$ tends to zero and the first term in Eq. (14) can be neglected. The equation becomes

$$\hat{E}\left(1-\frac{d\hat{E}}{d\hat{x}}\right)^{\gamma}=0\,. \qquad (16)$$

This equation reduces to the case of complete neglect of diffusion discussed in the first part of this section.

In the general case where $\alpha \neq 0$ and $\beta \neq 0$ the nonlinear boundary problem was solved numerically.[25] The results for various values of α and β in both the classical and quantum case are shown in Figs. 3 and 4. The effect of the limitation of charge on the screening is clearly demonstrated. The field penetration increases with increasing β (remember that these curves are normalized to E_0) and becomes nearly complete for $\beta=10$. For $\beta=10$ the field profiles are only weakly dependent on α. This means that for sufficiently high surface fields, the field profile does not change remarkably if the screening length decreases below the sample thickness. Comparing the field profiles for the classical and the quantum case we note a slightly better field penetration in the quantum case for lower values of α and β. The reason is that because of the Pauli exclusion principle, electrons cannot be as strongly concentrated in states with lower momentum values as in the classical case. This results in more intensive thermal motion of the quantum gas and, consequently, in a less strong screening. For higher values of α and β the difference between the classical and the quantum case disappears, since the diffusion becomes less important.

The above detailed calculations refer only to the floating, or isolated, boundary conditions. The effectiveness of the field penetration in the grounded case again depends on the values of α and β, but in addition, there is a fundamental asymmetry introduced between the results for the two polarities of the applied field. If the applied field is such as to produce an accumulation of electrons, β may be considered to tend to zero. Then if $\alpha > 1$, the screening length is less than the film thickness, and the field will drop to zero before reaching the front surface. If $\alpha < 1$ there will be field penetration to the front surface.

The more interesting case occurs when the external field produces a *depletion* in the film. In this case, β becomes the important factor in the field penetration since the positive charges are assumed to be immobile. Thus if $\beta > 1$, the free electrons are expelled from the film and the field penetrates to the surface. The value of α now affects only the details of the shape of the electric field profile, not the overall field penetration. This complicates the calculation, since the value of the electric field at the surface $\hat{x}=1$ is unknown. However, a self-consistent calculation can be performed by demanding the equality

$$4\pi\int_0^L \rho(x)dx=E_0-E_1 \qquad (17)$$

be satisfied. This can be accomplished by first assuming an initial slope $(dE/dx)_x=0$, performing the numerical calculation to find the value of E_1 at the surface of the film, and then performing the integration in Eq. (17) and checking for the equality in the expression. It is clear that if $\beta > 1$ in the case if depletion, the field can penetrate through the film even in the grounded case.

Several assumptions have been made to obtain the results of this section. The three main assumptions are, first, that the net current passing through the sample is zero, second, that the sample is electrically neutral, and third, that the number of free charges is independent of the applied field.

All of the assumptions are violated to some degree in an actual experiment. In the following, we examine the importance of deviations from the

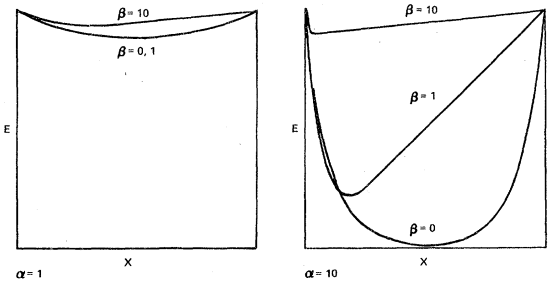

FIG. 4. Field profiles for various values of α and β for a quantum electron gas.

assumed conditions and determine the limitations of the theory and the experimental technique.

To estimate the influence of the nonvanishing net current on the field and charge density profile in the metal, we must compare the net current with the diffusion and Ohmic currents in Eq. (7). Both the latter currents are larger by orders of magnitude than a net current controlled by the conduction mechanisms discussed above. Therefore, we conclude that the field and charge density profile is not essentially changed by a real net current different from zero. This does not mean, however, that there cannot be other effects of a nonvanishing net current that must be considered, as is discussed later.

Secondly, we have assumed that the sample is electrically neutral. A loss of neutrality may result if the insulator-metal transition forms a blocking contact. Electrons from the insulator will then be injected into the metal. However, since the density of conduction electrons in an insulator is of the order of $10^3/\text{cm}^3$, the number of electrons available for injection, even for a very thick insulator, is small compared to the number of electrons in a metal sample of 100 Å thickness. Therefore, the effect is very small and may be neglected.

The last condition, that the number of free charges in the material is independent of the applied field, means that there should be no trapping or generation of electron-hole pairs caused by the electric field within the metal. At positions where the charge density is high, there are no localized states due to the static screening of the crystal imperfections. Trapping of free electrons in the depletion region is not effective because the number of free electrons is small and the localized states are ionized to a large extent by the strong electric field. Therefore, we conclude that field-dependent trapping or generation of free carriers through localized states can be ruled out as an efficient mechanism for field-dependent change of the number of free carriers within a metal.

Electron-hole pairs can be generated in two different ways in the metal sample. Electrons injected from the insulator conduction band into that of the metal will be hot electrons and they can create electron-hole pairs by collisions with valence-band electrons if their energy exceeds the threshold energy for impact ionization. An electron-hole pair density different from zero will occur only if a current flows from the insulator into the metal and therefore can be reduced by making the net current small.

The more important generation process of electron-hole pairs is tunneling of electrons from the valence band into the conduction band of the metal. Interband tunneling becomes important if the potential drop in the metal sample over a distance l (which is either the mean free path length or the sample thickness, depending on which is smaller), becomes comparable to the energy separation between the valence band top and the Fermi level. If the characteristic tunneling length l is assumed to be approximately 100 Å, the threshold value of the mean electric field strength for tunneling becomes 10^6 to 10^7 V/cm. Above this value interband tunneling becomes an efficient generation process of free electrons and holes. Both kinds of free carriers give an additional contribution to the screening of the electric field.

The question is, can the experimental requirements be met? There are several difficulties encountered in obtaining the extremely high electric fields while simultaneously suppressing the free-carrier reflectance effects.[26] As was discussed earlier, the basic requirement is to produce a surface charge density sufficient to exceed the product of the sample thickness and carrier density. This requirement can be met by some ferroelectric materials.

When a thin slab of a ferroelectric material is polarized normally to its faces and the polarizing field is removed, a surface charge remains in the electrodes that is equal to the remnant polarization of the ferroelectric. These large induced fields can be used to study the ER of a conductor, if one of the electrodes is composed of the material of interest.

The sample is evaporated in the form of a thin film onto a polished slab of ferroelectric ceramic. The ferroelectric is permanently polarized to avoid problems involved in switching,[27] including luminesence and time-dependent strains. To produce a signal proportional to the difference in reflectivities, the experimental package is divided into two regions of different polarization. A spatial reflectometer compares the two regions by moving the sample back and forth under the focussed beam from the monochrometer.

A second approach is to use a barrier effect instead of a ferroelectric. The sample film can be isolated by locating it between two capacator plates and a voltage applied across the entire sample. This package has several advantages. It can be fabricated entirely in a vacuum by successive evaporations without exposure to air. The symmetry of the package guarantees neutrality, in that substantial amounts of charge cannot accumulate on the sample. Conventional (not spatial) modulation techniques can be used. If breakdown occurs, it is clearly indicated. However, the fields are limited to the breakdown conditions in the insulating barrier. This breakdown lies be-

TABLE I. Maximum values of film thickness for the condition $\sigma \geq \rho_0 L$ in a degenerate electron gas.

ρ_0 (cm^{-3})	$P = 0.3$ μC/cm^2	$P = 30$ μC/cm^2	d_{TF} (Å)
10^{16}	20 μm	200 μm	7.9
10^{18}	200 Å	2 μm	3.6
10^{20}	2 Å	200 Å	1.7
10^{22}	<<1 Å	2 Å	0.8

tween 10^6–10^7 V/cm for good-quality evaporated insulators such as Al_2O_3 or SiO_2 producing a field in the metal much below that generated by a ferroelectric.

The choice of experimental approach to obtain band-structure-specific ER information depends primarily on the free-carrier concentration in the material of interest.

In order to obtain significant field penetration in realistic materials, the saturation condition must be approached. The maximum values of sample thickness for the saturation condition $\sigma \leq {}_0 l$ are given in Table I. The thickness and the Thomas-Fermi screening lengths are given as a function of free-carrier density for two different surface charge conditions that correspond roughly to the field values obtainable by the ferroelectric and surface-barrier techniques. It can be seen that at metallic carrier densities the thicknesses for saturation are unrealistic from an experimental point of view. However, for materials with carrier densities in the semimetal range of 10^{18}–10^{20} cm^{-3}, it appears feasible to eliminate the free-carrier effects and obtain ER data characteristic of the band structure of the material.

A second consideration is that the surface of the sample probed by the light must be fully depleted to eliminate the free-carrier effects. In practical terms this means that there must be a bias field large enough to force the free carriers away from the reflecting surface.

IV. SUMMARY

The basis for this study was derived from the hypothesis that a static electric field could penetrate into a thin conducting film if the total number of carriers available for terminating the electric field lines was less than the number of field lines.

We have developed a theory for the electric field penetration into a metal, and calculated the carrier distribution and electric field profiles for real materials. A differential equation governing the field variation was obtained by utilizing the condition of equilibrium between electric and diffusion currents. The numerical solution indicates that the expected carrier depletion can result in a deep penetration of the electric field into a conducting film. The calculations also show the importance of isolating the sample from external sources of electrons in order to produce a field penetration throughout the thickness of the sample.

During the course of the study we have encountered some fundamental limitations on the upper values of applied fields for this application. These limitations apply, in particular, to materials that have free carrier densities in excess of about 10^{20} cm^{-3} and make the application of the ER as a band structure probe in metals doubtful. However, the techniques developed during this study open up meaningful ER measurements to a wide range of materials, including highly doped semiconductors, semimetals, and some alloys.[28]

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[1] J. Feinleib, Phys. Rev. Lett. 16, 1200 (1966).

[2] J. D. E. McIntyre, Surf. Sci. 37, 658 (1973).

[3] T. E. Furtak, and D. W. Lynch, Phys. Rev. Lett. 35, 960 (1975).

[4] A. Prostak, and W. N. Hansen, Phys.Rev. 160, 600 (1967).

[5] M. Stedman, Chem. Phys. Lett. 2, 457 (1968).

[6] M. Stedman, Symp. Faraday Soc. 4, 64 (1970).

[7] J. D. E. McIntyre, *Advances in Electrochemistry and Electrochemical Engineering, Optical Techniques in Electrochemistry*, edited by R. H. Muller (Wiley, New York, 1973), Vol. 9, p. 61.

[8] J. D. E. McIntyre, and D. E. Aspnes, Bull. Am. Phys. Soc. 15, 366 (1970).

[9] R. Garrigos, R. Kofman, and J. Richard, Solid State Comm. 14, 1029 (1974).

[10] J. Tauc, Prog. Semicond. 9, 83 (1965).

[11] R. Enderlein, in *Proceedings of the 12th International Conference on the Physics of Semiconductors*, edited by M. Pilkuhn (Teubner, Stuttgart, 1974), p. 161.

[12] M. Cardona, *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. E. Ehrenreich (Academic, New York, 1969), Suppl. 11.

[13] N. Bottka and D. L. Johnson, Phys.Rev. B 11, 2969 (1975). B. O. Seraphin, in *Semiconductors and Semi-*

metals, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1972), Vol. 9.

[14] D. E. Aspnes and A. Frova, Solid State Commun. 7, 155 (1969).

[15] J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. 24, 417 (1971).

[16] R. P. Howson, J. Avaritsiotis, and T. Fox, Thin Solid Film 30, 297 (1975).

[17] R. Garrigos, Ph.D. thesis (L'Universite de Nice, France, 1974) (unpublished).

[18] P. Cheyssac, R. Garrigos, R. Kofman, L. Pénavaire, J. Richard, and A. Saissy, Surf. Sci. 37, 683 (1973).

[19] B. O. Seraphin, in *Optical Properties of Solids*, edited by F. Abeles (North-Holland, Amsterdam, 1972).

[20] N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).

[21] D. M. Newns, Phys. Rev. B 1, 3340 (1970).

[22] D. E. Beck and V. Celli, Phys. Rev. B 2, 2955 (1970).

[23] H. F. Budd and J. Vannimenus, Phys. Rev. B 12, 509 (1975).

[24] V. L. Bouch-Bruevich, J. P. Sviagyn, and A. G. Mironov, *Domennaia Elekricheskaia Neustoicherost V Poluprovodnikakh* (Nauka, Moscow, 1972), p. 82.

[25] J. D. Rancourt, Ph.D. thesis (University of Arizona, 1974) (unpublished).

[26] A. J. Hunt (unpublished).

[27] Y. Ishibashi and H. L. Stadler, J. Phys. Chem. Solids 30, 2113 (1969).

[28] T. L. Liu, Phys. Rev. B 12, 3008 (1975).