Monte Carlo Calculations Pertaining to the Transport of Hot Electrons in Metals*

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Monte Carlo calculations are applied to the problem of "hot" electron motion in metals, and measured values of attenuation length, L, are related to values of the mean free paths for electron-electron scattering l_e, and electron-phonon scattering l_p. Calculations are done for both specular and diffuse reflectance of electrons at the boundaries of the metal films and for values of the average loss per electron-phonon collision, ΔE_p, of 0.001, 0.01, 0.02, and 0.03 eV. If the values of l_p obtained from conductivity measurements are used, the following values or limits are found for l_e using experimentally determined values of L for electrons with excess energies about 0.9 eV: Au, $l_e>4000$ Å; Ag, $l_e=900$ Å, and Pd, $l_e=900$ Å. These results are compared with the theory of Quinn.

I. INTRODUCTION

THERE are a number of processes by which hot electrons in solids may be scattered. Examples are electron-electron and electron-phonon scattering. One popular and effective experimental method of studying the scattering processes is to measure the attenuation length, L, for hot electrons.[1,2] The attenuation length is defined in terms of the probability $P(x)$ of electrons excited at a distance x from a barrier (see Fig. 1) escaping over that barrier.[1] The escape probability is assumed to be given by

$$P(x) \propto e^{-x/L}. \quad (1)$$

The barrier may be that between two solids, e.g., a metal-semiconductor junction, or a solid-vacuum barrier. With the latter configuration, attenuation lengths have been measured using photoemission[3] or secondary electron emission[4] techniques. A large amount of data has recently been obtained on metals by using the former configuration.[1,2] In these experiments, the thickness of the metal of interest is varied between a few hundreds and thousands of angstroms. Radiation incident on the metal film (Fig. 1) then excites electrons. After undergoing a number of scattering events, some of these electrons reach the metal-semiconductor interface with sufficient momentum to surmount the energy barrier. By measuring the current collected at the barrier as a function of the sample thickness, the attenuation length can be determined.

The attenuation lengths must be related to the fundamental scattering processes through the scattering parameters (mean free path, energy loss, and scattering angle) for each process. Only if this is done is it possible to make comparisons between measured attenuation lengths and theoretical[5–7] calculations of the scattering parameters. The difficulty in obtaining mean free paths from attenuation lengths by analytical methods arises

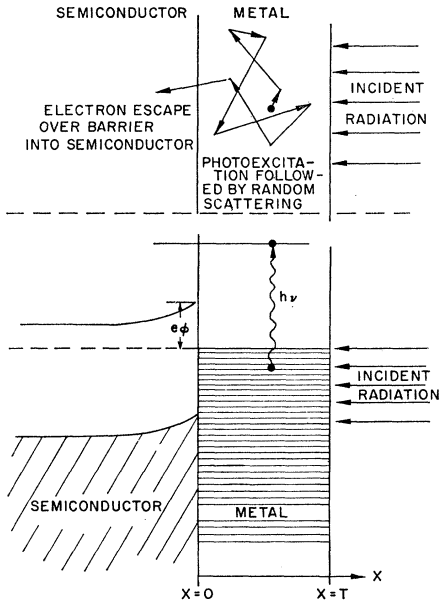

FIG. 1. Top: Two-dimensional spatial diagram illustrating photoemission from a metal into a semiconductor. Bottom: Photoemission from a metal into a semiconductor in terms of an energy-band diagram.

* Work performed under the auspices of the U. S. Atomic Energy Commission and the Advanced Research Projects Agency through the Center for Materials Research at Stanford University.

[1] G. W. Spitzer, C. R. Crowell, and M. M. Atalla, Phys. Rev. Letters **8**, 57 (1962). C. R. Crowell, W. G. Spitzer, L. E. Howarth, and E. E. LaBate, Phys. Rev. **127**, 2006 (1962).

[2] J. L. Moll and S. M. Sze (to be published).

[3] J. A. Burton, Phys. Rev. **72**, 531(A) (1947). W. E. Spicer, RCA Review **19**, 555 (1958). W. E. Spicer, Phys. Chem. Solids **22**, 365 (1961).

[4] A. J. Dekker, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 251.

[5] J. J. Quinn, Phys. Rev. **126**, 1453 (1962).

[6] J. J. Quinn, Appl. Phys. Letters **2**, 167 (1963).

[7] M. S. Sparks and K. Motizuki (to be published).

from the fact that neither diffusion nor age theory[2,8] is completely adequate for problems in which the initial source is located within a few mean free paths of the surface, as is usually the case in these experiments. However, as has been well demonstrated in the treatment of similar problems in neutron physics, the problem can be treated as accurately as desired by application of the Monte Carlo method.[9] It is the purpose of this paper to report on such calculations.[10] These calculations have been tailored to fit the experiments currently being made on metals by Crowell, Spitzer, and their coworkers,[1] and by Sze and Moll.[2] The calculations have been made in such a way that they should have more general applicability.

The problem treated here has three facets. First, values must be assigned to the various parameters involved in the problem such as the scattering mean free paths and the energy distribution of the excited electrons. Then, the problem must be programmed for a digital computer and the computations carried out. Finally, the results must be compared to experiment and interpreted.

II. CALCULATIONS

A. Physical Model and Assignment of Parameters

The parameters which must be assigned in the present problem are concerned with: (1) the photoexcitation of carriers, (2) the scattering of excited carriers, and (3) the escape of carriers over the potential barrier.

The optical absorption producing "hot" carriers was assumed to follow the usual exponential law, and an absorption coefficient α of 7.7×10^5 cm^{-1} was used. This is the coefficient for Au in the near infrared and is close to that of the other metals in that wavelength range. The choice of the optical absorption coefficient is only critical when the attenuation length is comparable to or less than the mean absorption depth. When it is necessary to take into account a different value for α, this can be done by multiplying L and the scattering lengths by 7.7×10^5 cm$^{-1}/\alpha$, where α is the new value for the absorption coefficient.

The electrons excited to energies greater than the barrier height were assumed to be distributed uniformly in energy. Upon excitation, the momentum of the electrons was assumed to be distributed isotropically in direction. A few cases were examined in which the energy of the incident photon was added entirely to the "normal component" of the electron's initial energy; the result was a change in photoelectric yield but a negligible change in calculated attenuation length.

The scattering events can be divided into bulk and surface scattering. Surface scattering occurs when electrons strike either the metal-air or metal-semiconductor interface with insufficient momentum to escape. Calculations have been made for both specular and diffuse surface reflections. In the former case, the angles of incidence and reflectance are equal; in the latter case, the reflected electrons follow Lambert's law. It was assumed that no energy loss is associated with surface scattering.

Several types of scattering events may occur in the volume of the material. The first of these is electron-electron scattering. In this case, the excited electron will lose a large fraction (roughly half) of its energy in excess of the Fermi energy.[5,11] Since the maximum electron energy was taken to be only a few tenths of an eV above the barrier energy, it was assumed that an electron has zero escape probability after it suffers such a scattering event.

Lattice scattering must also be considered. Here an electron can either gain or lose the phonon energy E_p in a single collision, depending upon whether a phonon is emitted or absorbed. Thus the average energy loss per collision will be less than E_p. The phonon energy E_p is also restricted according to the relationship $E_p\approx k\theta$, where k is Boltzmann's constant and θ is the Debye temperature. Complete calculations were made for energy losses of 0.001, 0.01, 0.02, and 0.03 eV. (The value[12] of $k\theta$ for Cu is 0.029 eV, whereas that for Au is 0.0136 eV.)

It is necessary to also consider scattering due to defects or impurities in the crystal. Since the energy loss due to such scattering can be expected to be negligible, the only effect of this type of scattering would be to change the direction of motion of the carrier. This and anisotropic scattering in general can be taken into account in an approximate manner by assuming two types of scattering events, which when averaged over many events would approximate the actual scattering. The first scattering mechanism would be isotropic and the second would be completely forward. If the average energy loss per collision for forward scattering is given by $\Delta E'$, such scattering can be taken into account by replacing the average energy loss per collision ΔE_p by

$$\Delta E_p\left(1+\frac{l_{pi}}{l_{pf}}\frac{\Delta E'}{\Delta E_p}\right), \tag{2}$$

where l_{pi} is the electron-phonon mean free path for isotropic scattering and l_{pf} is that for forward scattering. The electron-phonon scattering mean free path used remains that for isotropic scattering. In a later section, values of the electron-phonon mean free paths obtained

[8] B. Davison, *Neutron Transport Theory* (Oxford University Press, New York, 1958).

[9] See, for example, E. D. Cashwell and C. J. Everett, Los Alamos Scientific Laboratory Report No. LA-2120, 1957 (unpublished).

[10] Preliminary results have been reported previously. See R. N. Stuart, F. Wooten, and W. E. Spicer, Phys. Rev. Letters **10**, 7 (1963).

[11] P. A. Wolff, Phys. Rev. **95**, 56 (1954).

[12] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), pp. 4–48.

from conductivity data will be used. Since forward scattering is not important in determining the conductivity, the use of these data is appropriate.

B. Monte Carlo Program Description

The basic assumptions used in the calculations were outlined in the preceding section. In this section, the application of these assumptions to the Monte Carlo method will be described.

The initial source distribution of electrons $S(X,E)$ in the film was generated by computing for each electron an initial energy E and position X. The initial energy E was determined from

$$E=E_F+h\nu-(h\nu-e\phi)u_1, \tag{3}$$

where $e\phi$ is the barrier height with respect to the Fermi energy E_F, $h\nu$ is the photon energy, and u_1 is a random number, $0\leq u_1\leq 1$. Thus only values of E in the range $E_F+e\phi\leq E\leq E_F+h\nu$ are considered, i.e., only electrons initially excited to an energy at least equal to the minimum energy for escape. Equation (2) assumes that the probability of an electron being excited to a state with energy between $E_F+e\phi$ and $E_F+h\nu$ is independent of the energy of the states involved.[13]

The initial position X (see Fig. 1) was determined from

$$X=T+(1/\alpha)\ln\{1-u_2[1-\exp(-\alpha T)]\}, \tag{4}$$

where T is the film thickness, α is the optical absorption constant, and u_2 is a random number, $0\leq u_2\leq 1$. The above equation for X was found by setting the area under the absorption curve, i.e., the integral $N\int_T^{T-X} e^{-\alpha(T-X)}dX$, equal to a random number u_2 after first having normalized the total area, $N\int_T^0 e^{-\alpha(T-X)}dX$, to unity. By this means, the exponential spatial distribution of the optical absorption was taken into account.

Having selected an initial position and energy, the next step was to find the distance the electron would travel before undergoing a collision. The probability of going a distance l or greater is given by $\exp(-l/l_T)$ where the total mean free path, l_T, is related to the mean free path for electron-phonon scattering, l_p, and the mean free path for electron-electron scattering, l_e, by the equation $l_T=l_el_p/(l_e+l_p)$. Setting the normalized integral $(1/T)\int_l^\infty e^{-l/l_T}dl$ equal to a random number u_3, $0\leq u_3\leq 1$, and solving for l, the distance traveled is found to be

$$l=l_T|\ln u_3|. \tag{5}$$

The angle θ at which the electron travels initially with respect to the normal to the metal-semiconductor interface is found in accordance with the assumption that the initial direction is isotropic. Thus all solid angles $d\Omega$ are equally probable. This is easily shown to be equivalent to all values of $\cos\theta$ being equally probable, so that $\cos\theta$ was found from the equation

$$\cos\theta=2u_4-1, \tag{6}$$

where u_4 is a random number, $0\leq u_4\leq 1$.

Finally, it was necessary to decide what sort of scattering event terminated the initial path of the electron at distance l. The probability of undergoing an electron-electron collision, for example, is equal to the cross section for such scattering divided by the total cross section for all scattering events. Since, except for surface boundary scattering, only electron-electron and electron-phonon scattering was considered, a random number u_5, $0\leq u_5\leq 1$, was chosen such that *if*

$$u_5<\frac{1/l_e}{1/l_p+1/l_e}=\frac{l_T}{l_e}, \tag{7}$$

the scattering was taken to be electron-electron scattering. Otherwise, it was taken to be electron-phonon scattering. The appropriate energy loss was then recorded.

In a similar fashion, the new trajectory, the coordinate for the next collision, and the energy loss were computed. The process was repeated until the electron either escaped or dropped to an energy below that of the barrier. The entire process was then repeated until at least 10 000 calculations were made for each set of parameters. Calculations of the yield were always made for at least five values of film thickness, namely, 200, 400, 600, 800, and 1000 Å. These thicknesses were chosen for convenience of comparison with the experimental data. For short values of the attenuation length, however, the number of electrons escaping from a 1000 Å film was frequently too small to be of significance. All yields referred to in the present paper are with respect to electrons initially excited to an energy state above the barrier. Thus, a correction must be made to obtain absolute rather than relative quantum yields. The extrapolated yield Y_0 is the yield extrapolated to zero thickness using the attenuation length which best fits the Monte Carlo calculations for the thickness range 200–1000 Å.

The probability of escape after a collision, for an electron having sufficient momentum perpendicular to the barrier, is

$$P_{i,n}=\exp(-X/l_T\cos\theta), \tag{8}$$

where i is a collision index, n is an electron index, and $X/\cos\theta$ is the distance traveled along the trajectory if the electron is headed toward the barrier. If, for example, the electron is headed toward the metal-air interface and specular reflection is assumed, then X is replaced by $X-2T$. A tally was made of both the actual number of electrons which escaped, N_e, and the probable number of escapes

$$N_e'=\sum_{i,n}P_{i,n}. \tag{9}$$

[13] R. A. Smith, *Wave Mechanics of Crystalline Solids* (John Wiley & Sons, Inc., New York, 1961), p. 345.

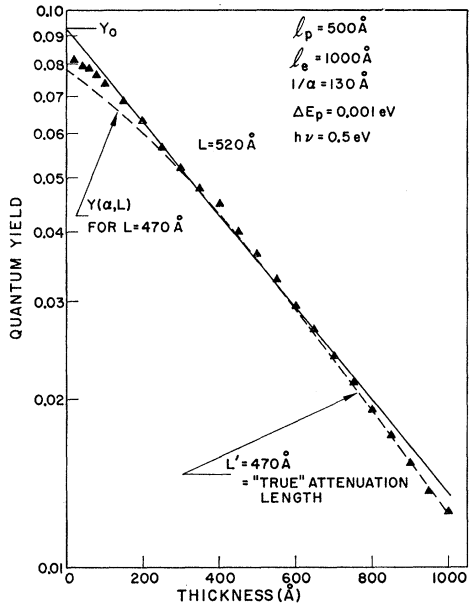

FIG. 2. Calculated quantum yield versus thickness for specular reflectance. The solid line is the best fit for thicknesses from 100 to 600 Å. The dashed curve is the best fit of Eq. (11) to thicknesses greater than 500 Å.

The standard deviation of N_e' is

$$\left[\sum_n\left(\sum_i P_{i,n}\right)^2-\frac{(N_e')^2}{N}\right]^{1/2}, \tag{10}$$

where N is the total number of electrons considered. The standard deviation indicated that N_e' is a somewhat more accurate number than N_e, although the two quantities almost always differed by less than the standard deviation.

The results presented here are for $h\nu-\phi=0.225$ eV (corresponding to $h\nu=1.015$ eV and $\phi=0.79$ eV in the work reported for Au).[1] In practice, it was found that substantially the same value of L was obtained using $h\nu-\phi=0.31$ or 0.162 eV although the quantum yield changed appreciably.

III. RESULTS

A. Specular Boundary Reflectance

Over 250 curves of yield versus thickness have been calculated for the various values of the parameters involved. Since space clearly does not allow for the presentation of all of these curves, it was necessary to find a method for transmitting the maximum information in a minimum of space. In doing this, it was our purpose to provide information in a form which clearly illustrates the salient features of the results and also affords maximum usefulness for experimentalists wishing to interpret their own data.

In order to aid in the evaluation of the calculations, one set of calculations was made for a much larger number of thicknesses and with much better statistics than it was practical to use routinely. The results of these calculations, in which $l_e=1000$ Å, $l_p=500$ Å, and $\Delta E_p=0.001$ eV are presented in Fig. 2, where the yield is plotted versus sample thickness. The yield is in terms of the fraction of the excited electrons which are collected across the barrier. The trajectories of 100 000 electrons were followed for each point in Fig. 2. Thus Fig. 2 represents the results of 2.3×10^6 individual calculations. It was not feasible to make this number of calculations for each choice of parameters; therefore, the rest of the calculations were done for only five thicknesses (200, 400, 600, 800, and 1000 Å) and 10 000 trajectories were followed for each thickness. The results of these calculations of the attenuation length L for various values of the electron-phonon mean free path l_p, the electron-electron mean free path l_e, and the average energy loss ΔE_p have been plotted in Figs. 3 and 4.

All of the points in Fig. 2 do *not* lie on a straight line. To determine L, a straight line must be fitted to these data. The value of L obtained will differ depending on the portion of the curve to which the straight line is fitted. Because of the difficulties involved in obtaining data for larger thickness, the experimental values of L have most often been determined for thicknesses between 100 and 600 Å. The solid line in Fig. 2 is fitted to the points within these limits. It gives $L=520$ Å. Since it coincides most closely with the determination of L made by experimental workers, this method of deter-

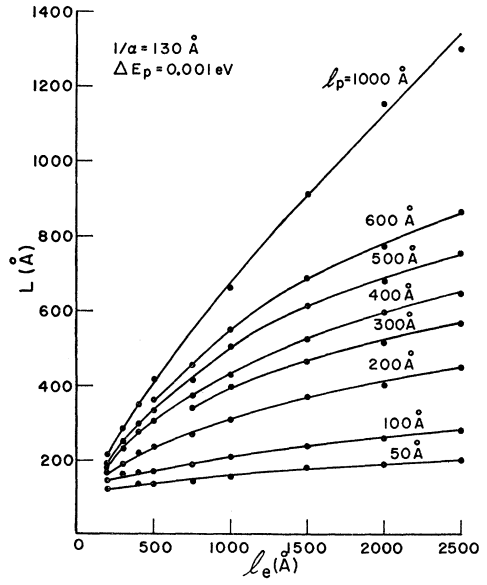

FIG. 3. Attenuation length L versus mean free path for electron-electron scattering l_e for various values of the electron-phonon mean free path l_e. Calculations were made on the basis of specular reflectance and an average energy loss, ΔE_p, of 0.001 eV per electron-phonon collision.

mining L has been adopted here. Approximating the curve by a straight line, the yield at any thickness can be determined if L and Y_0 are given. Y_0 is the intercept of the straight line on the ordinate. The values of Y_0 are reported in the Appendix.

A more accurate method of determining L exists. The method makes use of an equation[1] which relates the yield to α, L, and the thickness:

$$Y=K\frac{\alpha L}{\alpha L-1}\frac{(e^{-T/L}-e^{-\alpha T})}{(1-e^{-\alpha T})}. \tag{11}$$

K is constant for a given $h\nu$ and T is the sample thickness. No correction was made for electron scattering at the boundaries in deriving Eq. (11). For $L>1/\alpha$, a

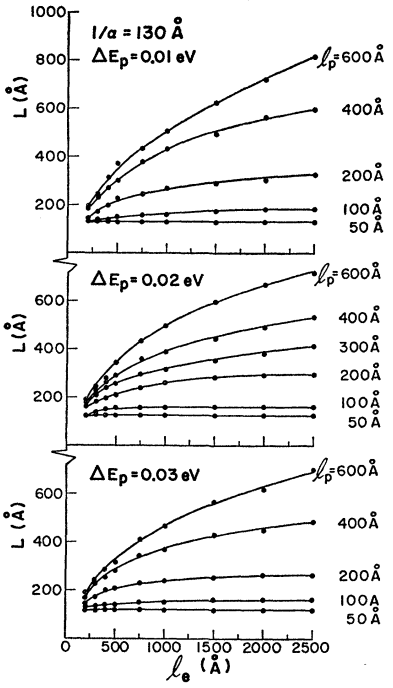

FIG. 4. Attenuation length L versus mean free path for electron-electron scattering l_e for various values of electron-phonon mean free path l_e and energy loss ΔE_p. Calculations were made on the basis of specular reflectance.

sufficiently large thickness can always be found such that

$$d(\ln Y)/dT=-1/L. \tag{12}$$

For smaller thickness, $d(\ln Y)/dT<-1/L$ due to the finite depth of optical absorption.

The dashed curve in Fig. 2 corresponds to $L=470$ Å, the value obtained from the slope of calculated points for $T\geq 500$ Å. The portion of the curve for $T<500$ Å was then obtained from Eq. (11) using $L=470$ Å. For $T<500$ Å, the yield falls below that obtained from the Monte Carlo calculation. This is probably due to the fact that multiple reflection of excited electrons from the boundary surfaces was not considered in deriving Eq. (11). Note that the "true" attenuation length,

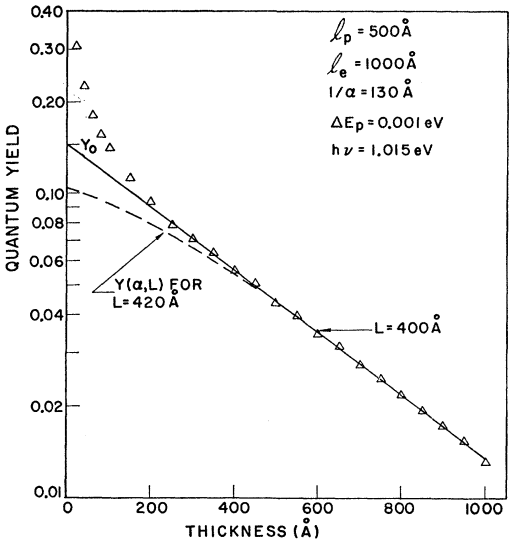

FIG. 5. Calculated quantum yield versus thickness for diffuse reflectance. The solid line is the best fit for thicknesses from 200 to 1000 Å. The dashed curve represents Eq. (9) and uses a corrected value of attenuation length L.

found above by fitting an exponential to calculated yields for $T\geq 500$ Å, is 50 Å less than the attenuation length of 520 Å found by fitting for $T<600$ Å. It was found in general that for specular boundary reflectance the value of L obtained by matching a straight line to

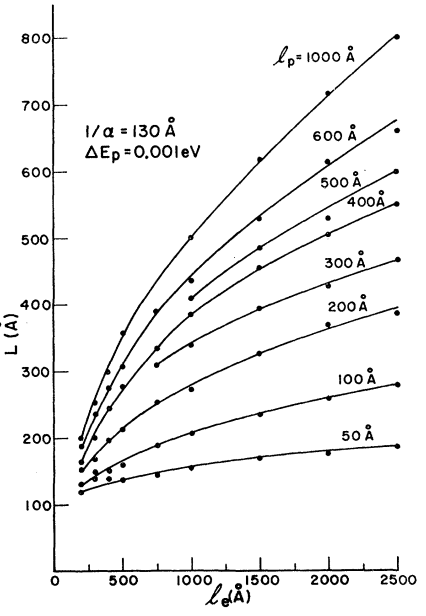

FIG. 6. Attenuation length L versus mean free path for electron-electron scattering l_e for various values of mean free path for electron-phonon scattering l_p. Calculations were made on the basis of diffuse reflectance and an energy loss ΔE_p of 0.001 eV per electron-phonon collision.

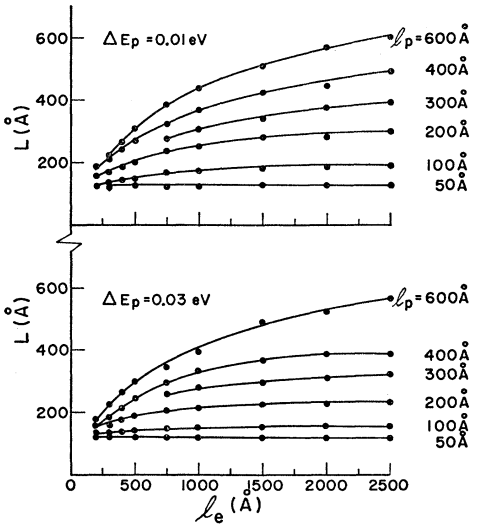

FIG. 7. Attenuation length L versus mean free path for electron-electron scattering l_e for various values of mean free path l_p and energy loss ΔE_p for electron-phonon scattering. Calculations were made on the basis of diffuse reflectance.

the yield for $T<600$ Å was higher by 50 ± 10 Å than the "true" value of L obtained through the use of Eq. (11).

B. Diffuse Reflectance

The yields for diffuse reflectance, with $l_p=500$ Å, $l_e=1000$ Å, and $\Delta E_p=0.001$ eV, were calculated for 50 thicknesses, ranging from 20 to 1000 Å. In these calculations, 10^5 test electrons were again used for each point. The data are presented in Fig. 5. Since, as with specular reflectance, it was impractical to make similar calculations for all combinations of values of the other parameters, calculations were again made for thicknesses of 200, 400, 600, 800, and 1000 Å using 10^4 electrons for each thickness and the best exponential fit was made to these points.

The difference between these data and those for specular reflectance is striking. Whereas the yields for specular reflectance fall below the straight line fit at small values of thickness, the diffuse data rises well above it for these thicknesses. This is reasonable, since diffuse reflectance at the surface opposite the barrier can increase the scattering of electrons into the escape cone. The importance of this effect will increase as the sample thicknesses decrease.

The data obtained for diffuse reflectance at the surfaces are presented in terms of L and Y_0, defined by the best straight line on a log plot fitted to the points at 200, 400, 600, 800, and 1000 Å. In the range where L becomes comparable to $1/\alpha$, a correction needs to be made because the slope of the yield curve depends on the absorption detph [see Eq. (11)]. The corrections are: for $L>200$, -20 ± 10 Å; for $L<200$, -30 ± 15 Å.

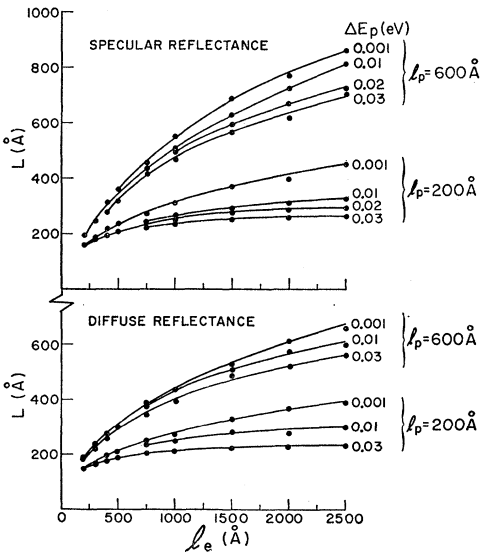

FIG. 8. Effect on attenuation length L of average energy loss ΔE_p for electron-phonon collisions.

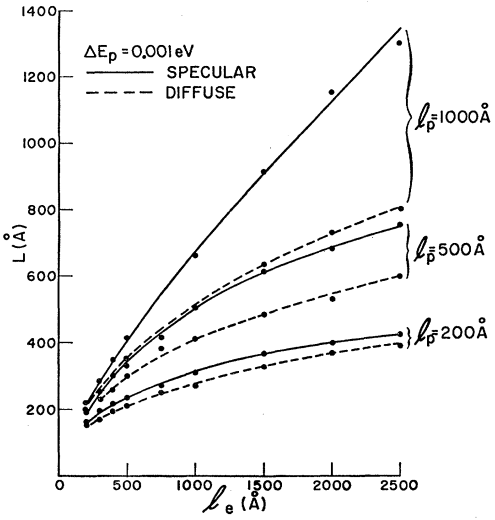

FIG. 9. Effect of reflectance on attenuation length L for various values of electron-phonon mean free path l_p.

In Fig. 6, values of L obtained directly from the Monte Carlo calculation, with $\Delta E_p=0.001$ eV, are plotted versus l_e for various values of l_p for diffuse reflectance at the boundaries. In Fig. 7, similar plots are given for $\Delta E_p=0.01$, 0.02, and 0.03 eV. For the sake of comparison, plots of L versus l_e are given in Fig. 8 for all values of ΔE_p and for $l_p=100$ and 600 Å. Since the dependence of L on ΔE_p was small for $l_p=600$ Å, the calculation for $l_p=1000$ Å was made only for $\Delta E_p=0.001$

eV. Plots of Y_0 versus l_e for the various values of parameters are included in Appendix I.

IV. DISCUSSION OF RESULTS

In the limit $l_p \gg l_e$, only electron-electron scattering need be considered. In such a case, only those electrons initially within the escape cone can possibly escape. For energies not far above threshold, the escape cone is small, so that only those electrons approaching the barrier at near normal incidence can escape. Thus, in the limit $l_p \gg l_e$, the attenuation length should approach l_e as $h\nu$ approaches $e\phi$.

In the other limit, where $l_p \ll l_e$, the attenuation length should approach that given by age theory,[2] except for the effects due to boundary scattering and phonon energy loss which cannot easily be introduced into an age theory treatment. The value of the Monte Carlo method lies in its ability to relate L to l_e and l_p in the regions between these two limits and to determine the effect of boundary conditions and energy loss due to phonon scattering. Since age theory provides the only analytically simple method of examining these problems, the results of age theory will be compared with those from the present Monte Carlo calculations in a later section. In this section, particular attention will be paid to the effects of the boundary conditions and phonon energy loss.

In Fig. 8, the plots of L versus l_e are given for l_p values of 200 and 600 Å for specular and diffuse reflectance. As would be expected, the effect of ΔE_p is greatest for the smaller value of l_p and large values of l_e. For $l_p = 200$ Å and $l_e = 2500$ Å, L is reduced by about a factor of 2 when ΔE_p is increased from 0.001 to 0.01 eV. However, for $l_p = 600$ Å the decrease is less than 20%. For $l_p > 600$ Å the effect of ΔE_p was found to be negligible. For $l_p > 200$ Å and for $\Delta E_p = 0.001$ eV, it was found that a negligible number of electrons are lost due to the degradation of their energy by phonon collisions; therefore, the change in L with increasing ΔE_p is a measure of the importance of this loss.

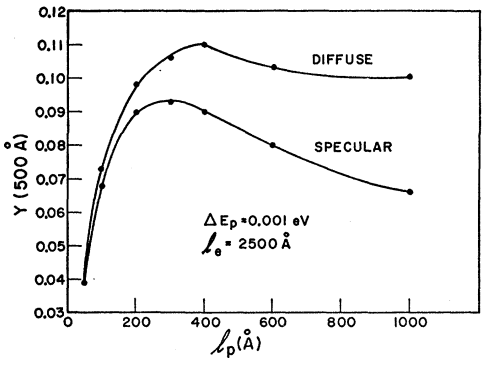

FIG. 10. Effect of reflectance on yield (for a film thickness of 500 Å) as a function of mean free path l_p for electron-phonon scattering. Calculations were made for an energy loss ΔE_p of 0.001 eV per electron-phonon collision and a mean free path l_e of 2500 Å for electron-electron scattering.

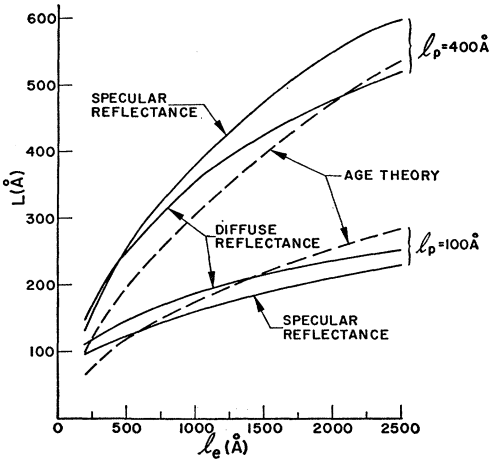

FIG. 11. Comparison of corrected Monte Carlo calculations with age theory for l_p values of 100 and 400 Å.

The importance of the reflectance in determining L is indicated in Fig. 9. The difference is greatest for large l_p and l_e. This can be understood in terms of scattering of electrons into the escape cone.[14] Only a small fraction of the electrons will be excited with their direction of motion initially within the escape cone. However, either scattering in the volume or diffuse reflectance at the back surface may place the direction of motion of an electron within the escape cone. Thus diffuse reflectance, but not specular reflectance, can increase the yield at small thickness and thus decrease L in regions where volume scattering events become infrequent.

When l_p is due to phonon scattering, it will be a function of the sample temperature. The yield as a function of l_p for a fixed thickness may be obtained for any thickness in the range 200–1000 Å by using the data given here. The yield for a thickness of 500 Å is plotted as a function of l_p in Fig. 10 for both diffuse and specular reflectance with $l_e = 2500$ Å and $\Delta E_p = 0.001$ eV. The yield for specular reflectance increases with increasing l_p until it reaches its maximum value when $l_p \approx 300$ Å; then it decreases as l_p increases. The decrease is due to the fact that as l_p increases there are less scattering events which will scatter electrons *into* the escape cone. However, diffuse reflectance continues to scatter electrons into the escape cone even when the phonon scattering becomes small. As a result, there is a large region over which the yield is almost independent of l_p. If l_p varied over this range as the temperature was varied, the yield would be almost independent of temperature.

[14] R. H. Fowler, Phys. Rev. 38, 50 (1931).

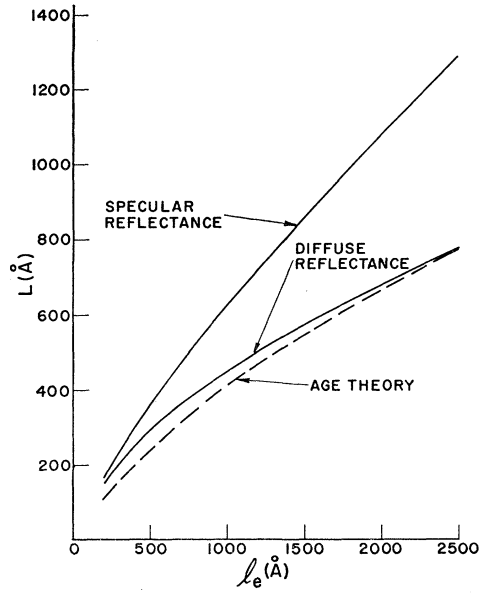

FIG. 12. Comparison of corrected Monte Carlo calculations with age theory for $l_p = 1000$ Å.

V. COMPARISON WITH AGE THEORY

Age theory[2] gives an asymptotic relationship between L, l_e, and l_p:

$$L(E) = [l_e^2 l_p / 3(l_e + l_p)]^{1/2}. \quad (13)$$

This expression was derived using certain assumptions:

(1) that the initial source is located many attenuation lengths from the surface;

(2) that the scattering associated with l_p is elastic;

(3) that $l_p \ll l_e$.

These assumptions are rarely fulfilled in the situations for which the Monte Carlo calculations were made. However, the Monte Carlo calculations can only be done on a computing machine, whereas Eq. (13) can be applied very easily. As a result, it would be useful to know the errors involved in applying age theory in the case examined here. This error investigation can be done by comparing the results obtained from the Monte Carlo calculations with those obtained from Eq. (13). This is done for three values of the parameters in Figs. 11 and 12.

TABLE I. Mean free paths and attenuation lengths for electrons approximately 0.9 eV above the Fermi level. l_p is the electron-phonon mean free path determined from conductivity [Ref. 2 and N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958) p. 268]. L is the measured attenuation length (Refs. 1, 2) for energies above the Fermi level (in eV) as given in parenthesis. ΔE_p is the average energy loss per electron-phonon collision at 300°K. l_e is the electron-electron mean free path deduced from the experimental L using the values of l_p and ΔE_p indicated in the table. The value in parenthesis was obtained by assuming a value of l_p one-half of that given in the table. l_e (diffuse) and l_e (specular) indicate the results obtained by use of diffuse and specular reflection, respectively, at the boundaries. The column labeled "Calc l_e" gives the results of Quinn (Ref. 5). The values in parenthesis are those corrected by Quinn to take into account the effect of shielding by d-band electrons.

Material	l_p (Å)	L (Å)	ΔE_p at 300°K (eV)	Electron-electron mean free path (Å) l_e (diffuse)	l_e (specular)	Calc l_e
Au	406	740	0.0037	>4000	3000	415
		(0.8–1.0)		(>8000)	(>6000)	(910)
Ag	570	410	0.007	900	650	560
		(0.65–0.95)		(3000)	(2400)	(1000)
Cu	420	50–200	0.015	<300	<200	720
		(0.55–0.95)		(<500)	(<400)	(1700)
Pd	110	170	0.0096	~900	~900	...
		(0.7–0.8)		(>5000)	(>5000)	

VI. COMPARISON WITH EXPERIMENTAL DATA

Crowell *et al.*[1] have measured the attenuation length for electrons with energies above the Fermi energy between approximately 0.6 and 1.0 eV in Au, Ag, Pd, and Cu using the method described in the Introduction. The electron energies and barrier heights in these experiments closely parallel those used for the calculations reported here. Moll and Sze[2] have made similar measurements on Au for electron energies close to 0.8, 1.0, 1.3, 1.6, 1.9, and 4.7 eV. To a good approximation, the dis-

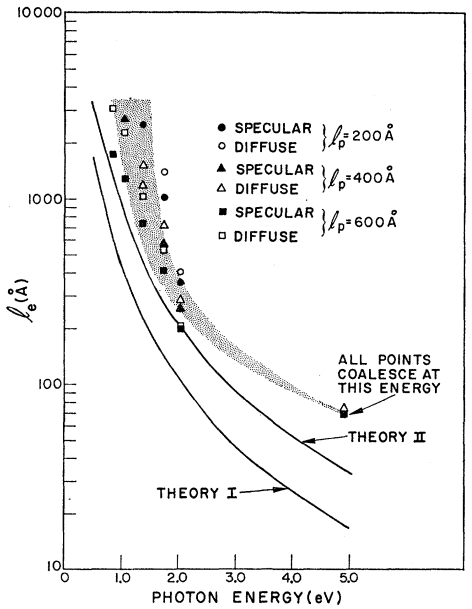

FIG. 13. The points indicate values of the electron-electron mean free path l_e obtained from the experimental data on Au (Refs. 1 and 2) by use of the Monte Carlo calculations for three values of l_p and both diffuse and specular boundary scattering. The curve labeled Theory I is from the original theory of Quinn (Ref. 5). Theory II includes the modification made by Quinn in his theory to take into account the effect of shielding by d-band electrons.

tribution in energy of the excited electrons enters the problem only as the difference in energy between the excited electrons and the potential barrier over which they must escape.[15] This energy difference did not vary appreciably between the experiments of Moll and Sze and these calculations. As a result, it is appropriate to use these Monte Carlo calculations to analyze their data.

The principal purpose of this analysis is to obtain the mean free path for electron-electron scattering l_e from the data. In order to do this, a value must be assigned to l_p. From conductivity measurements, values of l_p are available. These, of course, pertain to electrons near the Fermi surface. Values for the materials of interest here are given in Table I. Moll and Sze[2] have recently confirmed the l_p value of Au using evaporated samples. For electrons with energies well in excess of the Fermi energy, the values of l_p may be somewhat different; however, it is unlikely that they will be in excess of those at the Fermi level. Imperfections in the evaporated film will reduce l_p.

The values of l_e obtained from the data of Moll and Sze[2] are plotted in Fig. 13 versus the energy of the incident photons. Values of l_e were obtained (see Figs. 3 and 6) for l_p values of 200, 400, and 600 Å (the value obtained from conductivity data is 400 Å) and for both specular and diffuse reflectance. ΔE_p was taken to be 0.001 eV. The values of L obtained by Crowell *et al.*[1] near 1.0 eV are in agreement with those of Moll and Sze.[2]

As is to be expected (see Sec. IV), the value of l_e is insensitive to l_p at high energies, but is sensitive to l_p for large values of l_e (low values of energy). Despite any uncertainty in l_p, it is clear that l_e becomes much larger than 1000 Å for energies less than 1.0 eV above the Fermi energy. As the electron energy increases, l_e decreases, reaching values of about 70 Å for 5 eV. However, since it is very difficult to measure L for $L<1/\alpha$ by the techniques used by Moll and Sze,[2] the possible error in this case is large.

The value of L obtained for electron energies near 0.9 eV by Crowell *et al.* are presented in Table I. The values for ΔE_p given in Table I were obtained using the approximate relation

$$\Delta E_p = k\theta\{2[\exp(\theta/T)-1]^{-1}+1\}^{-1}. \quad (14)$$

The values of l_e for diffuse and specular reflectance given in Table I were obtained from the experimental attenuation lengths by the Monte Carlo calculations using the values of l_p given in Table I. These values of l_p may be high; therefore, values of l_e were also obtained by using values of l_p one-half of those given in Table I. These are given in parenthesis in Table I.

For Cu, it is highly probable, as Crowell *et al.* have pointed out, that the films contained oxygen contamination which produced additional scattering centers. If l_e for Cu was as long as that for Au, a reduction of l_p by a factor of 5 or 10 could produce the low attenuation length measured by Crowell *et al.*

The case for Pd is particularly interesting. The measured value of attenuation length is much less than that for Au or Ag; however, this can be explained on the basis of the reduced value of l_p (see Table I) provided that l_p for excited electrons and those at the Fermi level are the same. It should also be pointed out that because of the insensitivity of L to l_e for such low values of l_p, it is very difficult to determine l_e from the experimental data. The value of 900 Å given in Table I should be considered only a first approximation. Crowell *et al.*[1] place an uncertainty of ±30 Å on their value of L. The lower value of L, 140 Å would give $l_e=400$ Å; the upper value, 210 Å, would give $l_e=3000$ Å.

VII. COMPARISON WITH THEORY

The values of l_e obtained from the theory of Quinn[5] by Crowell *et al.*[1] are given in the last column of Table I. In Fig. 13, the values of l_e obtained from that theory have been plotted (labeled Theory I).

As Quinn has pointed out,[6] his original theory was based on the free electron model and did not take into account the screening contribution of the d-band electrons. Quinn has recently modified his original theory for Ag and Cu to take this screening into account. The modified values of l_e are given in parenthesis. The modification of l_e for Ag brings it in much closer agreement with the experimentally determined value. The similarity between the optical properties of Au and Cu in the visible region suggests that the d band in Au is also located about 2.0 eV below the Fermi level and that the d-band correction factors of Quinn[6] for Cu and Au should be almost identical. A second curve has been plotted (labeled Theory II) in Fig. 13 in which such a correction has been made. The corrected curve falls near the lower limit of the experimentally determined values for l_e.

Quinn has suggested[6] that if it is not due to imperfections in the film, the low value of l_e may be due to the scattering of excited electrons by electrons in some portion of the d band which lies within 0.55 eV of the Fermi surface. However, recent photoemissive measurements[16] of the d-band density of states indicate that the d-band edge does, in fact, lie 2.0 eV below the Fermi energy as Ehrenreich and Philipp deduced from optical data.[17]

VIII. CONCLUSION

For electrons in metals with energy of approximately an electron volt in excess of the Fermi energy, the Monte Carlo calculations indicate that the electron-electron scattering lengths are much longer than the experi-

[15] See, for example, R. H. Fowler, Ref. 14.

[16] W. E. Spicer and C. N. Berglund (unpublished).

[17] H. Ehrenreich and H. R. Philipp, Phys. Rev. **128**, 1622 (1962).

mentally determined attenuation lengths. These calculations also indicate the strong dependence of the attenuation length on the scattering length for elastic or almost elastic events such as those due to phonons and lattice imperfections. They also show that, to a lesser extent, the attenuation length is affected by the type of reflectance and the average energy loss per lattice scattering. The low value l_e obtained for Cu can be explained in terms of scattering due to oxygen contamination. The values of l_e obtained for Au as a function of energy are in qualitative agreement with the original theory of Quinn[5] based on a free-electron model but, quantitatively, those theoretical results are too low. The Coulombic shielding of the d-band electrons seems to be an important factor in producing the long mean free paths. Quinn has modified his free-electron theory to take this into account.[6] The corrected theory is in fairly good agreement with the measured values (see Fig. 11).

For electrons with energy E, the d-band electrons can only contribute to the electronic screening and thus increase l_e as long as $E-E_F<E_F-E_d$, where E_F is the Fermi energy and E_d is the maximum energy in the d bands. However, for $E-E_F>E_F-E_d$ the d-band electrons will also serve as scatterers. Thus the electron-electron mean free path should drop appreciably as $E-E_F$ becomes greater than E_F-E_d. In materials like Pd where E_F-E_d is small or zero, the net effect of the d-band electrons may be to reduce l_e even for small values of $E-E_F$.

There is need for attenuation length data from materials such as aluminum in which there is no d band which overlaps the conduction band. If such data were available, Quinn's original theory[5] could be tested more closely and, by comparison with the materials studied previously, the effects of the d bands more clearly illuminated. However, the experience with Cu indicates that great care must be taken with sample preparation in order to avoid contamination.

There is also a need to obtain better values for l_p, the electron-phonon mean free path, before exact values of l_e can be determined from attenuation length measurements. Temperature studies might help here. However, for materials which have large values of l_p at room temperature, diffuse reflectance at the boundaries will mask the effect of increased l_p (see Figs. 9 and 10); in these cases, only an increase in temperature and thus decrease in l_p could effectively change the attenuation length.

Comparison of the Monte Carlo results with those obtained from age theory[2] (see Fig. 11) indicates that there is rarely more than a factor of 2 difference in these results.

ACKNOWLEDGMENTS

We wish to thank Professor John Moll for some stimulating conversations. One of the authors (W. E. Spicer) wishes to acknowledge useful conversations with E. K. Gatchell.

APPENDIX

In Figs. 14 through 17, values of Y_0 obtained by extrapolation (see Sec. III) are given. Note that Y_0 is a strong function of ΔE_p for small l_p.

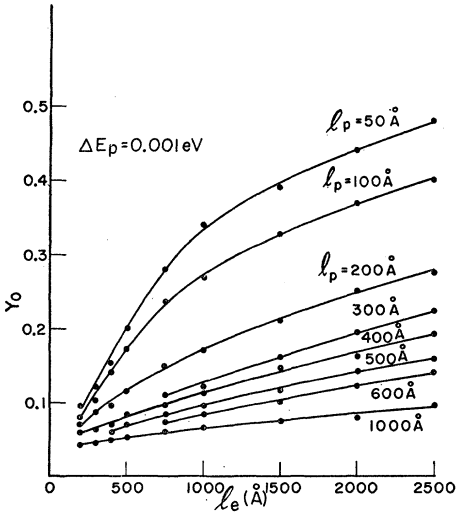

FIG. 14. Quantum yield extrapolated to zero thickness Y_0 for specular reflectance with $\Delta E_p=0.001$ eV.

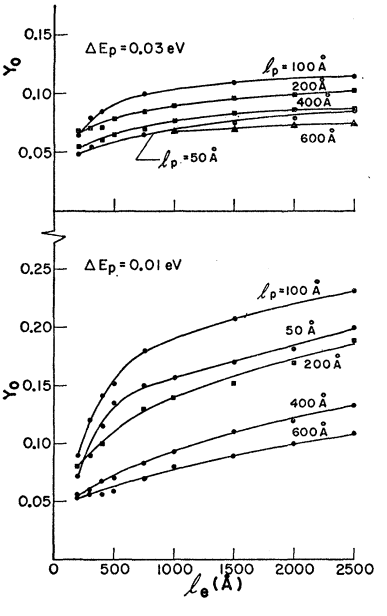

FIG. 15. Quantum yield extrapolated to zero thickness Y_0 for specular reflectance with ΔE_p values of 0.01 and 0.03 eV.

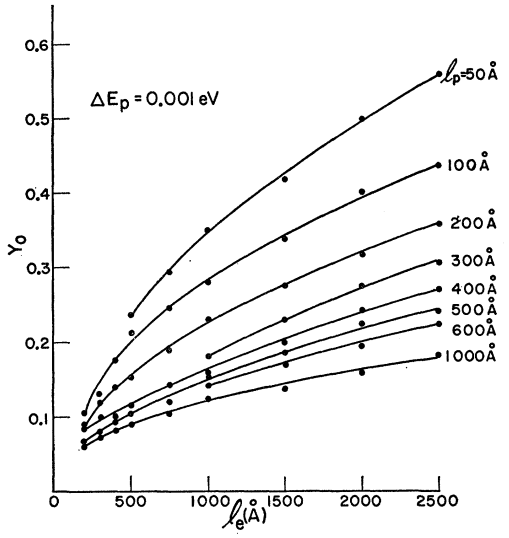

FIG. 16. Quantum yield extrapolated to zero thickness Y_0 for diffuse reflectance and $\Delta E_p = 0.001$ eV.

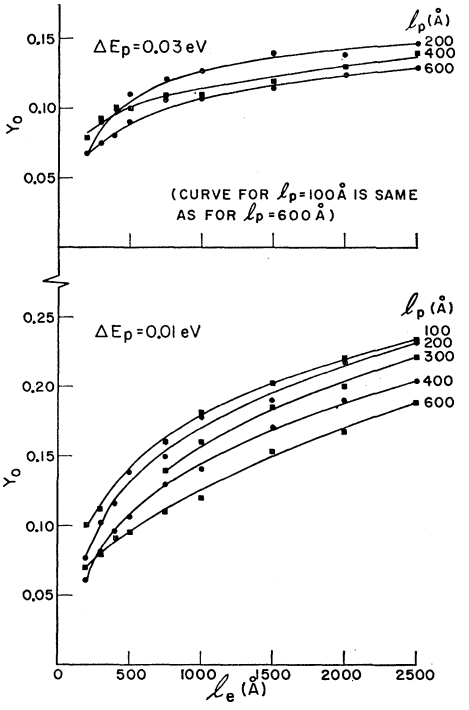

FIG. 17. Quantum yield extrapolated to zero thickness Y_0 for diffuse reflectance with ΔE_p values of 0.01 and 0.03 eV.

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Scattering of Electrons by Vacancies in Nonstoichiometric Crystals of Titanium Carbide*

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A study has been made of the influence of carbon vacancies on the resistivity of titanium carbide, a refractory hard metal. Crystals were obtained with vacancies in concentrations of from 3 to 20%. The vacancies were introduced into the fcc carbon sublattice of the rock salt structure of TiC by controlling the C/Ti ratio during crystal growth. The vacancy concentration in some crystals was further reduced by preferential vaporization of Ti at high temperatures and in others by addition of ~1% boron to release carbon to the lattice through the formation of TiB_2 precipitates. Measurements were then made of resistivity as a function of vacancy concentration at 77 and 298°K. On some samples, the Hall coefficient was also measured. The resistivity shows a monotonic increase with increasing vacancy concentration and has a large residual value, whereas the Hall coefficient is relatively independent of vacancy concentration but increases at low temperatures. The data are analyzed using Matthiessen's rule and the Bloch-Grüneisen formula and interpreted using Mott's band model for transition metals. A value for the added resistivity per atomic percent carbon vacancies in TiC was obtained: 16$\mu\Omega$ cm. This value is an order of magnitude larger than that for the noble metals. A four part explanation is offered: TiC has a smaller number of conduction electrons per atom, the scattering probability is higher in TiC because of the high density of states in a *d*-like band overlapping the *s*-like conduction band, the screening of a vacancy is less effective because of the smaller number of conduction electrons, and the effective charge of a vacancy is probably greater than 1*e*. The room-temperature resistivity of stoichiometric TiC, as inferred in the analysis, is 70±10 $\mu\Omega$ cm.

1. INTRODUCTION

FUNDAMENTAL investigations of the properties of the refractory hard metals are hampered by the difficulty of obtaining pure and well-characterized samples. A survey of data on the room-temperature resistivity of titanium carbide indicates that fourteen different investigators have obtained values ranging from 35 to 250 $\mu\Omega$ cm. The rather surprising lack of agreement for the value of this simple quantity was one

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