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Fowler's Hypothesis and the Determination of Photoemission Thresholds*

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It is shown that Fowler's hypothesis to explain photoemission from metals is not necessary to obtain a spectral dependence of quantum yield near threshold that varies as $Y^{\frac{1}{2}} \propto (h\nu - e\phi)$. It is not possible to distinguish between a Fowler distribution and an isotropic distribution of excited electrons even if rather extreme cases of electron scattering are included. As a result, knowledge that photoemission from a metal follows a Fowler plot does not permit any inferences regarding the nature of the initial excitation.

IT is common practice to determine the work function of metals by means of a plot of $Y^{1/2}$ versus $h\nu$, where Y is the yield in electrons emitted per photon absorbed, and $h\nu$ is the photon energy.[1-3] The result is usually a straight line whose intercept with the $h\nu$ axis gives the work function $e\phi$. Such plots are based on a model for photoelectric emission originally introduced by Fowler.[1] We shall refer to such plots as Fowler plots even though the term is also used to describe the particular form of temperature-dependent yield plot presented in Fig. 3 of Fowler's paper.[1] By repeated use over the years since Fowler's paper appeared, his hypothesis to get agreement with photoelectric experiments has attained the status of the Fowler theory of photoemission. Fowler plots are sometimes used even for semiconductors,[4] and often the result is indeed linear; but of what significance is such a result? In short, what can one infer from the knowledge that the quantum yield of a material follows a Fowler plot?

We want to point out here why a Fowler plot usually works so well for metals, why it sometimes works well for semiconductors, and why little physical significance can be inferred from either case.

Fowler's concern was with the effect of temperature in smearing out the photoelectric threshold. He wanted to find a simple method of determining the true threshold of metals at all temperatures. He experimented with several hypotheses. The one which worked best assumed that the quantum yield is proportional to the number of electrons per unit volume of the metal *whose kinetic energy normal to the surface augmented by hν is sufficient to overcome the potential step at the surface*. He called this number the number of available electrons.

Fowler made an explicit calculation of the number of available electrons for a free-electron gas at a finite temperature. He included the temperature dependence of the number of available electrons by means of the Fermi-Dirac distribution function.

There can be no quarrel with the use of Fermi-Dirac statistics for an electron gas; it is quite necessary if smearing of the Fermi surface is to be included in the model. However, Fowler's model is now most often used in the zero-temperature limit. It is a plot of this limiting function which is now commonly used to determine photoelectric thresholds.[2,3]

If the electrons in a free-electron gas are distributed isotropically after excitation, the escape probability of an electron with energy E is

$$\begin{aligned} P(E) &= \Omega(E)/4\pi \\ &= \tfrac{1}{2}[1-(E_0/E)^{1/2}], \end{aligned} \qquad (1)$$

where $\Omega(E)$ is the solid angle included by the excape cone for electrons with energy E and E_0 is the height of the surface-energy barrier. The escape cone includes all those electrons with sufficient momentum normal to the vacuum surface to escape. The quantum yield is then

$$Y = \int_{E_0}^{E_m} N(E)P(E)dE\,, \qquad (2)$$

where $N(E)$ is the normalized distribution in energy of excited electrons, and E_m is the maximum energy to which an electron can be excited by a photon of energy $h\nu$.

Near threshold,

$$(E-E_0)/E_0 \ll 1\,, \qquad (3)$$

and if $N(E)$ is taken as constant, Eq. (2) can be integrated to give

$$Y \propto (E_m - E_0)^2 = (h\nu - e\phi)^2. \qquad (4)$$

This is precisely the dependence of yield on $h\nu$ that characterizes Fowler's model near threshold.

It is now clear that for a free-electron gas near threshold, it is not possible to distinguish between an isotropic distribution and a Fowler distribution of excited electrons on the basis of the spectral dependence of quantum yield. Both the Fowler hypothesis and the escape-cone argument for an isotropic distribution ignore the effects of electron scattering. To see if electron scattering can have an effect which discriminates between the two models requires a more sophisticated calculation. This is probably handled most easily by means of Monte Carlo calculations.

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A detailed description of the Monte Carlo calculations used can be found in previous publications.[5–7]

Calculations reported here were made for $E_0=8$ eV, $e\phi=4$ eV, and for both Fowler and isotropic distributions. For each distribution, two calculations were made. One assumed an electron-electron scattering mean free path comparable to the mean optical-absorption depth but no scattering by phonons. The other assumed an electron-phonon scattering mean free path comparable to the mean optical-absorption depth but no electron-electron scattering.

After an electron-electron scattering event, escape was no longer possible. However, an assumed energy loss of only 0.01 eV per electron-phonon collision often permitted many such collisions before escape was no longer possible. For example, an electron excited to 0.5 eV above the vacuum level could undergo 50 electron-phonon collisions before losing too much energy to escape.

A second set of calculations was identical to the first set except that the escape cone was calculated as if the band minimum were 4 eV below the vacuum level. This is simply a way of very crudely approximating the situation in semiconductors or more complex real metals in which electrons are excited from lower bands to higher ones which are free-electron-like.

The results of all these calculations are shown in Fig. 1. It is clear from Fig. 1 that even when rather extreme cases of scattering are included in the analysis it is not possible to distinguish between a Fowler distribution and an isotropic distribution of excited electrons near threshold.

The quantum yield for a Fowler distribution is approximately twice as great as for an isotropic distribution because all electrons have been given a component of momentum towards the vacuum surface, whereas for an isotropic distribution only half the electrons have a component of momentum towards the vacuum surface. The ratio is actually slightly greater than 2 because in a Fowler distribution all the photon energy goes into increasing the energy normal to the surface.

Note that whereas all energies are reported in eV, the units can be arbitrary. It is only ratios of energies and of mean free paths that are important in the calculations. Energy units have been chosen simply to correspond approximately to real values.

In Fowler's model, all the energy absorbed by an electron is used to increase the energy normal to the surface. One might infer from this that momentum is conserved by means of the surface, and in turn, that if photoemission from a metal follows a Fowler plot near threshold, then photoemission might be a surface effect. It is now clear that no such conclusions can be drawn. In fact, since even photoemission from semiconductors may follow a Fowler plot, it seems that the spectral dependence of the yield near threshold is for the most part just a consequence of the variation in escape cone with energy.

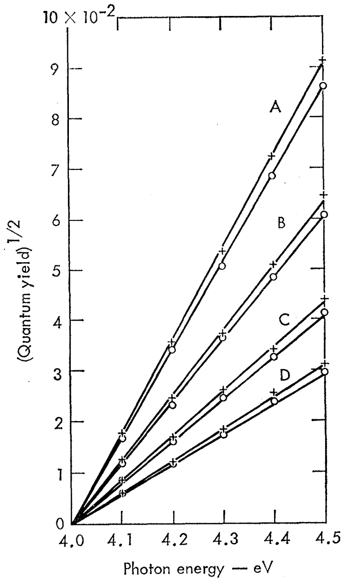

FIG. 1. Square root of quantum yield versus photon energy. In each of the four sets of curves, the upper curve is for electron-phonon scattering only and the lower curve is for electron-electron scattering only. Curve A represents Fowler distribution with escape cone calculated for band minimum 4 eV below vacuum level. Curve B represents Fowler distribution with band minimum 8 eV below vacuum level. Curve C represents isotropic distribution with escape cone calculated for band minimum 4 eV below vacuum level. Curve D represents isotropic distribution with band minimum 8 eV below vacuum level.

One factor which may considerably modify the spectral dependence of quantum yield is pronounced structure in the density of states. This is the main reason that semiconductors do not obey Eq. (4) near threshold. Some of these aspects of photoemission from semiconductors have been discussed in detail.[8,9] The pronounced effect that structure in the density of states of metals can have on quantum yield is demonstrated by data for copper with a monolayer of cesium.[2]

The calculations reported here were made for the zero-temperature limit of Fowler's model. The effect of a finite temperature is only to smear out the sharp cutoff at the high-energy end of the distribution of excited electrons. Thus the conclusions reached here hold also for the finite-temperature model of Fowler.

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