

## Theories of the Spectral Selective Photoelectric Effect

CLARENCE ZENER, *H. H. Wills Physics Laboratory, Bristol, England, and The Institute for Advanced Study, Princeton*

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Clean alkali surfaces emit less than one photoelectron for every 10,000 incident light quanta in the visible spectrum. A monomolecular layer of gas can greatly increase this yield. In this paper it is shown that mechanisms in which the metal electrons directly absorb the light can never give high efficiencies. A process is discussed in

which alkali atoms *outside* the gas layer absorb light, their excitation energy then being transferred to the metal electrons. This process is shown capable of giving an efficiency comparable with the highest which has been observed.

THE photoelectric efficiency of a metal frequently has a maximum in the visible spectrum, i.e., the efficiency is *spectral selective*.<sup>1</sup> The interpretation of this maximum has been the basis of considerable speculation. The models of three different theories are represented schematically in Figs. 1–3. The purpose of the present letter is to discuss the relative efficiency of these models. We conclude that the highest observed efficiency can be obtained only with the third model.

In the first theory the wall of the Sommerfeld free electron gas model acts as the third body which is necessary for the simultaneous conservation of energy and of momentum. The photoelectric yield of such a model has been the subject of numerous calculations.<sup>2</sup> The result pertinent to our discussion is that the efficiency at the peak is not greater than  $2 \times 10^{-4}$  (the efficiency is the reciprocal of the number of incident photons required for the ejection of one photoelectron). Although cases of such low efficiency have been observed, the efficiency at the peak may in certain cases be as high as 0.05.<sup>1</sup>

Campbell<sup>3</sup> has proposed that the most efficient surfaces are obtained when an alkali metal is covered first by a monomolecular layer of electronegative gas, then by a monatomic layer of alkali atoms. Fowler<sup>4</sup> suggested that the potential of such a surface, Fig. 2, would be such

as to allow the transmission of electrons having a normal velocity only within certain bands. The wide acceptance of this theory is surprising in view of the simplicity of the argument that may be advanced against it. Now when the selective effect is absent, as is apparently the case for clean surfaces,<sup>5</sup> the photoelectric efficiency is exceedingly low in the visible region,

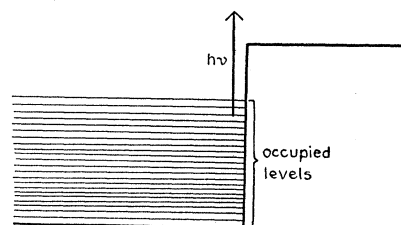


FIG. 1. Free electron model. The surface wall acts as the third body in the absorption of light quanta.

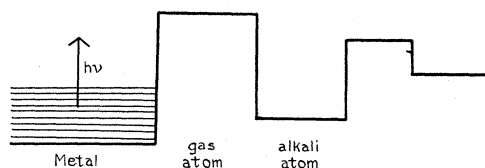


FIG. 2. Velocity filter model. Only electrons whose normal velocities lie within certain bands may escape from the metal.

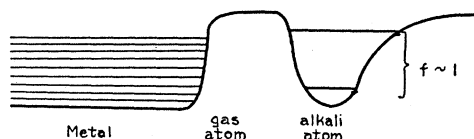


FIG. 3. Bound surface electron model. Electrons bound to the surface absorb the light, and then transfer their energy of excitation to metal electrons.

<sup>1</sup> A comprehensive review of the spectral selective effect is given by R. Suhrmann, *Ergebnisse der Exakten Naturwissenschaften* **13**, 148–223 (1934).

<sup>2</sup> G. Wentzel, *Sommerfeld-Festschrift*, 79 (1928).  
H. Frölich, *Ann. d. Physik* **7**, 109 (1930).  
I. Tamm and S. Schubin, *Zeits. f. Physik* **68**, 97 (1931).  
K. Mitchell, *Proc. Roy. Soc. A* **146**, 442 (1934).

<sup>3</sup> N. R. Campbell, *Photoelectric Cells and Their Applications* (London), p. 10, 1930.

<sup>4</sup> R. H. Fowler, *Proc. Roy. Soc. A* **128**, 123 (1930).

<sup>5</sup> Hughes and Dubridge, *Photoelectric Phenomena*, p. 160, 1932.

of the order of  $10^{-5}$ .<sup>1</sup> This low efficiency is due to the small number of electrons striking the surface with sufficient energy to escape, and is *not* due to a small reflection coefficient. This conclusion is reached upon observing that in the equation for the thermionic current

$$I = 120(1-r)T^2 e^{-\phi/kT} \text{ amperes cm}^{-2},$$

the reflection coefficient  $r$  of clean surfaces is found experimentally to be of the order of  $\frac{1}{2}$ .<sup>6</sup> A velocity filter at the surface can thus only *lower* the photoelectric efficiency on both sides of a band. The efficiency at a peak in the visible spectrum would thus be of the order of  $10^{-5}$ .

The idea has been advanced, particularly by Suhrmann,<sup>1</sup> that the light is absorbed by atoms isolated from the main body of the metal. A model for a monatomic layer of such atoms is schematized in Fig. 3. The constancy of the potential in the plane of the surface is the representation of the idea that the monatomic alkali layer forms a two dimensional alkali metal. For in the visible and near ultraviolet we know that the essential optical properties of the alkali metals may be obtained with a constant potential.<sup>7</sup> The nearly parabolic form of the valley insures us that the oscillator strength ( $f$  value) for the transition from the normal to the first excited state will be nearly unity. We assume essentially that the binding of an alkali atom to the surface does not appreciably affect its oscillator strength from the normal state to that resonance level corresponding to a vibration normal to the surface.

The process of photoelectric emission according to this model is the following. A surface electron absorbs a light quantum, thus being excited to the resonance level. The excitation energy is next transferred to an electron in the metal, which then escapes from the metal. We shall now calculate the efficiency of this model.

Let  $f$ ,  $\Delta\nu$ ,  $A$  be the oscillator strength, line breadth, and effective cross section at the center of an absorption line, respectively, for a transi-

tion of a single electron. Then

$$A\Delta\nu = (4e^2/mc)f = 0.034f.$$

Taking the line breadth to be such that  $h\Delta\nu = 1$  electron volt (approximately the breadth of the selective effect) and setting  $f = 1$ , we obtain the effective cross section at center of line to be  $0.14 \times 10^{-14} \text{ cm}^2$ . Hence a surface layer of  $7 \times 10^{14}$  electrons  $\text{cm}^{-2}$  may have an absorption line 1 electron volt broad with a maximum absorption efficiency of 0.1. Hence this third model can give an efficiency as high as has been observed.

The spectral selective effect is dependent upon the state of polarization of the incident light. For optically smooth surfaces no spectral selective effect is observed when the light is so polarized that the electric vector is parallel to the surface.<sup>8</sup> Irrespective of the model used, we must expect from optical considerations<sup>9</sup> that light so polarized will be less effective than light polarized so that the electric vector is in the plane of incidence. As the angle of incidence approaches  $90^\circ$ , the ratio of the square of the electric vector normal to the surface, for the second type of polarization, to the square of the electric vector (parallel to the surface) in the first type of polarization, is  $|\mathbf{n}^4|$  just at the surface of the metal, where  $\mathbf{n}$  is the complex refractive index of the metal.<sup>10</sup> In the visible region, this ratio is of the order of 100 for Pt, and of the order of 5 for K. This factor is not sufficient to explain the difference between the effects of the two types of polarized light for the highly efficient surfaces with K as a base. The model which we use must itself differentiate between electric fields normal and parallel to the surface. In our model the potential is constant along the surface, so that electrons in the outer trough behave as if free with respect to electric fields parallel to the surface.

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<sup>6</sup> R. H. Fowler, *Statistical Mechanics* (Cambridge), p. 268, 1929.

<sup>7</sup> C. Zener, *Nature* **132**, 968 (1933).

<sup>8</sup> Reference 5, p. 143.

<sup>9</sup> H. E. Ives, *Phys. Rev.* **38**, 1209 (1931).

<sup>10</sup> M. Born, *Optik* (Berlin), p. 260, 1933.