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Work-Function Estimation with a Single Yield Measurement*

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WORK functions are generally determined by means of the Fowler method,[1] which consists of fitting a series of relative photoelectric yield measurements (made at different values of incident photon energies) to a standard curve. In this communication, a simplified (but less accurate) method for estimating the work function of a material is discussed. The advantage of the method is that it requires only a single measurement of the absolute photoelectric yield, but it is made with an incident photon energy which is less than the photoelectric threshold energy. The simplification results from the relative insensitivity of the work-function determination to variations of the parameter α [see Eq. (1)] in this region of photon energy: therefore an approximate value of α may be used. (This results from the rapid decrease of the electron occupation density for states above the Fermi level.) The method, which evolved in the course of studying the double-quantum photoelectric effect in metallic sodium,[2] is based upon the Fowler theory of photoemission,[1] and is particularly suited to measurements of the work functions of metallic single crystals. Some experimental data for an evaporated sodium surface are presented.

Theory: The expression for the yield in the Fowler theory is[1,3]

$$Y=\alpha A T^2 \Phi(x), \qquad (1)$$

where α is the experimentally determined constant of proportionality, $A=4\pi mk^2/h^3$, T is the absolute temperature, and $\Phi(x)$ is the Fowler function. For photon energies ($h\nu$) below the photoelectric threshold energy ($e\phi$) the expression $\Phi(x)$ is given by

$$\Phi(x)=[e^x-e^{2x}/2^2+e^{3x}/3^2-\cdots], \quad x\leq 0. \qquad (2)$$

Here, $x=(h\nu-e\phi)/kT$ so that for $h\nu<e\phi$, only the first term in the above series need be considered, provided that $|h\nu-e\phi|\gg kT$. Thus to good approximation in this region,

$$Y\simeq \alpha A T^2 \exp[(h\nu-e\phi)/kT]. \qquad (3)$$

The expression for the work function may therefore be written

$$e\phi\simeq h\nu+kT\ln[\alpha A T^2/Y], \quad h\nu<e\phi. \qquad (4)$$

With a single yield (Y) measurement, and an arbitrary value for α (see *Discussion*), all of the parameters on the right-hand side of this equation are known. In particular, the frequency of the incident radiation is generally known with high accuracy.

Experiment: The method described has been used[2] to determine the work function of a vapor-deposited sodium surface within a photomultiplier tube. Two different radiation sources were used, both having photon energies below the work-function energy of the material: a GaAs semiconductor injection laser emitting at 8450 Å (1.48 eV), and a He–Ne gas laser emitting at 6328 Å (1.96 eV). The measurements were carried out at room temperature ($T=300$°K). The constant A has the value 7.5×10^{20} electrons/sec-deg^2-cm^2 in cgs units, and a typical value[4] for α is 4×10^{-32} cm^2-sec/quantum. Then, for the experimental conditions used, $\alpha AT^2\simeq 2.7\times10^{-6}$. The two experiments are considered separately below.

(a) Radiation at 8450 Å: Using the measured value for the single quantum yield Y(300°K, 8450 Å$)=1.7\times10^{-15}$ A/W (see Ref. 2), we obtain the work function from Eq. (4),

$$e\phi\simeq 1.48 \text{ eV}+0.025 \text{ eV}[\ln(2.7\times10^{-6}/1.7\times10^{-15})]$$

or (5)

$$e\phi(8450 \text{ Å})\simeq 2.01\pm0.03 \text{ eV}.$$

In this case, $(h\nu-e\phi)/kT\sim-20$ so that the required inequality is well satisfied.

(b) Radiation at 6328 Å: Using a He–Ne gas laser with an output power of approximately 0.7 mW, a current of 1.3×10^{-9} A was observed from the cathode[5] of the photomultiplier. Thus, Y(300°K, 6328 Å$)=1.9\times10^{-6}$ A/W, and

$$e\phi\simeq 1.96 \text{ eV}+0.025 \text{ eV}[\ln(2.7\times10^{-6}/1.9\times10^{-6})]$$

or (6)

$$e\phi(6328 \text{ Å})\simeq 1.97\pm0.03 \text{ eV}.$$

For radiation at 6328 Å, however, the condition $(h\nu-e\phi)<-kT$ is not quite satisfied since $(h\nu-e\phi)/kT\sim-0.5$. Nevertheless, both of these work-function determinations are in agreement with each other, and with the value 1.9 ± 0.1 eV obtained independently from a Fowler plot.

Discussion: The validity of the Fowler theory relies on the stationarity of all variables in comparison with the rapidly varying Fermi function (with energy and temperature). Because this condition may be satisfied for either a volume or a surface model of photoemission,[6] the Fowler theory cannot be used to distinguish between the two[7]; it is an approximation to both models in the region near threshold.[7,8] In general, therefore, the applicability of the above method is independent of the photoemission mechanism.

Only a rough value of the yield is necessary to estimate the work function quite accurately. Thus, the dependence of the photoelectric yield on the polarization and the angle of incidence of the incident radiation may be neglected. Furthermore, if the surface under investigation is within a photomultiplier tube, as is the case with the experiments performed here, the gain of the photomultiplier need not be known with high accuracy. Similarly, the calculated value of the work function is rather insensitive to the value of α used. This is especially true since the values of α do not differ too much from metal to metal.[3,9] *An uncertainty in α or in Y by a factor of* 100 *changes the work function by about* 0.1 *eV at room temperature.* The relative insensitivity of the work-function determination to variations of the parameters α and Y is seen to arise from the location of these parameters in the argument of the slowly varying logarithmic function. Thus, to first approximation in estimating the work function of any metal, a single, arbitrary value for $\alpha(\sim10^{-33}-10^{-32}$ cm^2-sec/quantum) may be generally used. This is not true for measurements with $h\nu > e\phi$, since the dependence of the work function on α is much stronger than logarithmic in that region.

Conclusions: A determination of the work function of a material by this method has the advantage that it entails only one measurement of the absolute photocurrent. The method is intended as a rapid and convenient procedure for work-function estimation, when the accuracy provided by a full Fowler plot is not necessary. For polycrystalline materials, the work function obtained by such a measurement will be that of the lowest-work-function crystallites, since these contribute most heavily to the photocurrent. For single crystals, of course, the work function obtained will correspond to the particular crystal face investigated. Since the incident photon energy is below the work-function energy of the material, the measured photocurrent will be small. It may be measured with an electrometer, or if necessary, with a phase-sensitive detector in conjunction with a modulated light source.

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[4] R. J. Maurer, Phys. Rev. **57**, 653 (1940).

[5] In fact, for incident radiation at 6328 Å, the single quantum contribution to the photocurrent from the Fermi tail was so large that it precluded observation of a *double-quantum* current. In this case, the current from the photocathode was measured directly.

[6] If a volume effect is responsible for the transitions, however, then for film thicknesses below a critical thickness d_{crit}, α depends on the thickness of the film [see H. Thomas, Z. Physik **147**, 395 (1957)]. That is, below d_{crit} (which is the depth of photoemission), α will increase approximately linearly with film thickness, corresponding to the amount of sample emitting. This effect is neglected.

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[8] A. Meessen, J. Phys. Radium **22**, 308 (1961).

[9] For example, $\alpha(\mathrm{Na}) \simeq 4 \times 10^{-32}$ cm^2-sec/quantum while $\alpha(\mathrm{Ba}) \simeq 2 \times 10^{-32}$ cm^2-sec/quantum (see Ref. 4).