of n, then

$$\tau = t/n. \tag{15}$$

Since for all practical purposes $B(t)=n$, $at=n_0$ there is obtained from Eq. (14)

$$n_0 = \frac{n-\eta}{1-(n-\eta)(\tau/t)}. \tag{16}$$

This is for all practical purposes equivalent to Eq. (8) as long as $a\tau$ is not very close to 1.

ACKNOWLEDGMENT

The grant of the Research Foundation of the Ohio State University and the support given by The Ohio State University Development Fund are greatly appreciated by the authors.

PHYSICAL REVIEW VOLUME 68, NUMBERS 1 AND 2 JULY 1 AND 15, 1945

Theory of Photoelectric Emission from Metals

H. Y. Fan
Radio Research Institute, National Tsing Hua University, Kumming, China

(Received May 18, 1945)

The theory of volume effect in photoelectric emission is developed. Formulae are derived for the rate of electron excitation and for the photoelectric yield. The calculated threshold frequencies for volume effect are 5.91×10^{14} and 5.69×10^{14} for sodium and potassium respectively. The estimated photoelectric yields for these metals are of the same order of magnitude as those calculated for surface effect and are comparable with those observed experimentally. The volume effect should not, therefore, be neglected except in the immediate neighborhood of the threshold frequency. Approxmate estimation indicates that light absorption of sodium and potassium in the visible and ultraviolet regions should be largely due to quantum excitation of electrons. Accurate calculation of electron excitation and absorption requires detailed knowledge of electron wave functions.

INTRODUCTION

THE theory of photoelectric emission from metals is usually based on Sommerfeld's model of free electrons for metals. Since a free electron cannot absorb the whole energy of a light quantum (the kind of absorption for photoelectric emission), it has been suggested that light absorption takes place only at the surface of the metal where the electrons are subject to the surface potential field. The phenomenon is then a surface effect.

Wentzel[1] takes into account the damping of the light wave and accredits it with enabling the free electrons in the metal to absorb the energies of the light quanta. In this picture light absorption takes place inside the metal and is a volume effect. It has, however, been shown by Bethe[2] that the order of magnitude of emission given by this picture is too small.

The free electron model is too crude. Actually the electrons in a solid are in a periodic potential field. They can therefore absorb energies of light quanta independent of the damping of the light wave. Tamm and Schubin[3] made a rough estimation of the frequency, at which emission due to such absorption should begin, showing that it is much higher than the ordinary threshold frequency. Thereupon volume effect is neglected in the subsequent developments of the theory of photoelectric emission. It is our purpose to investigate this volume effect due to the periodic potential field inside the metal.

DEVELOPMENT OF THE THEORY

The potential energy of an electron in the crystal lattice of a solid is periodic

$$V=\textstyle\sum_g V_g \epsilon^{-2\pi i g\cdot r}. \tag{1}$$

The electron wave function is then of the form

$$\psi_k = \epsilon^{ik\cdot r} u_k(r),$$

---

[1] G. Wentzel, *Probleme der Modernen Physik* (Sommerfeld Festschrift), p. 79.

[2] H. Bethe, *Handbuch der Physik* 24/2, p. 472.

[3] I. Tamm and S. Schubin, Zeits. f. Physik **68**, 97 (1931).

where $u_k(r)$ is a function having the same periodicity as the potential. Optical phenomena with such electrons have been discussed in many places.[4] Let the vector potential of the light wave in the metal be

$$A=A_\xi \cos 2\pi\nu\left(t-\frac{n\eta}{c}\right)=\tfrac{1}{2}\left[A_\xi\epsilon^{-2\pi i n\eta/c}\epsilon^{2\pi i\nu t}+A_\xi\epsilon^{2\pi i n\eta/c}\epsilon^{-2\pi i\nu t}\right].$$

The damping can be neglected, since within the thickness in which we are interested, the wave is not appreciably damped. The perturbation due to this light wave is $(eh/2\pi imc)A\cdot\nabla\Psi$. By using the method of variation of constants we get for an electron originally in the state k

$$a_{k,k'}=-\frac{eh}{4\pi imc}\left[\frac{\exp\frac{2\pi i}{h}(E_{k'}-E_k-h\nu)t-1}{E_{k'}-E_k-h\nu}C^{+}_{k,k'}+\frac{\exp\frac{2\pi i}{h}(E_{k'}-E_k+h\nu)t-1}{E_{k'}-E_k+h\nu}C^{-}_{k,k'}\right] \tag{2}$$

where

$$C^{+}_{k,k'}=\int\psi^{*}_{k'}A_\xi\epsilon^{2\pi i n\eta/c}\cdot\nabla\psi_k d\tau;$$

$$C^{-}_{k,k'}=\int\psi^{*}_{k'}A_\xi\epsilon^{-2\pi i n\eta/c}\cdot\nabla\psi_k d\tau.$$

As the wave-length of the light wave is much longer than that of the electron waves, we can neglect $2\pi n\eta/c$ compared with k and k', then

$$C^{+}_{k,k'}=C^{-}_{k,k'}=\mathcal{A}_\xi\int\psi^{*}_{k'}\frac{\partial\psi_k}{\partial\xi}d\tau$$

$$=\mathcal{A}_\xi\int\epsilon^{-i(k'-k)\cdot r}u^{*}_{k'}\frac{\partial u_k}{\partial\xi}d\tau=\mathcal{A}_\xi C_{k,k'}. \tag{3}$$

It has been pointed out by Kronig[5] that because of the periodic nature of the functions $u(r)$, this integral is zero unless

$$k'-k=2\pi g.$$

This gives definite relations between the original state and the excited states; the electron cannot be excited from one state into any arbitrary state.

The probability of excitation of an electron in state k is

$$\sum_g\frac{d}{dt}|a_{k,k+2\pi g}|^2$$

per unit time. The total rate of excitation, i.e., the total number of excited electrons per unit time, is

$$N=2\frac{\Omega}{8\pi^3}\sum_g\frac{d}{dt}\int\int\int|a_{k,k+2\pi g}|^2dk_xdk_ydk_z \tag{4}$$

where Ω is the volume of the metal. The integration is over all occupied states. At $T=0$°K the limits of integration are given by the surface of Fermi distribution. By changing coordinates, the integral can be written

$$\int\int\int|a_{k,k+2\pi g}|^2dudvdw,$$

where u and v are coordinates in the surface of constant energy difference

$$H=E_{k+2\pi g}-E_k-h\nu=0 \tag{5}$$

in the k space, and w is the coordinate perpendicular to this surface. Since $a_{k,k+2\pi g}$ has a strong maximum at $w=0$ due to the factor

$$\frac{\exp(2\pi i/h)(E_{k+2\pi g}-E_k-h\nu)t-1}{E_{k+2\pi g}-E_k-h\nu},$$

we may put the slowly varying factor

$$C_{k,k+2\pi g}=C_{k,k+2\pi g\,w=0}$$

in the integration with respect to w, and neglect the second term in $a_{k,k+2\pi g}$. We then get

$$\int|a_{k,k+2\pi g}|^2dw=\left(\frac{eh}{4\pi mc}\right)^2|\mathcal{A}_\xi|^2|C_{k,k+2\pi g}|^2_{w=0}\times\int\left|\frac{\exp(2\pi i/h)(E_{k+2\pi g}-E_k-h\nu)t-1}{E_{k+2\pi g}-E_k-h\nu}\right|^2dw.$$

The main contribution to this integral comes from near $w=0$. We may therefore extend the limits to $-\infty$ and $+\infty$ and put

$$E_{k+2\pi g}-E_k-h\nu=\nabla H_{w=0}w. \tag{6}$$

Carrying out the integration we get

$$\int|a_{k,k+2\pi g}|^2dw=\left(\frac{e}{2mc}\right)^2ht|\mathcal{A}_\xi|^2\frac{|C_{k,k+2\pi g}|^2_{w=0}}{|\nabla H|_{w=0}}.$$

---

[4] A. H. Wilson, *The Theory of Metals*, see references on p. 127.

[5] R. de L. Kronig, Proc. Roy. Soc. **A124**, 409 (1929).

Substituting this expression into (4) we get[6]

$$N=2h\frac{\Omega}{8\pi^3}\left(\frac{e}{2mc}\right)^2|\mathfrak{A}_\xi|^2\sum_g\int\int\frac{|C_{k,\,k+2\pi g}|^2}{|\nabla H|}dudv. \qquad (7)$$

The integration is over the portion of surface $H=0$ bounded by the intersection of this surface with the surface of Fermi distribution.

Not all excited electrons can be emitted. As the tangential components of k are continuous at the surface, on account of the continuity of wave function, the condition for an excited electron to be emitted is

$$E(k_x+2\pi g_x,\, k_y+2\pi g_y,\, k_z+2\pi g_z)$$
$$\geqq W+\frac{h^2}{8\pi^2 m}[(k_y+2\pi g_y)^2+(k_z+2\pi g_z)^2], \qquad (8)$$

where W is the potential energy of an electron outside the metal. The volume of the metal Ω being the product of the surface area and the thickness l, the emission current per unit surface area is

$$J=2eh\left(\frac{e}{2mc}\right)^2\frac{l}{8\pi^3}|\mathfrak{A}_\xi|^2$$
$$\times\sum_g\int\int\frac{|C_{k,\,k+2\pi g}|^2}{|\nabla H|}dudv, \qquad (9)$$

where the integration is over that part of the surface $H=0$, which is bounded by the intersections of this surface with the surface of Fermi distribution and the surface (8).

Effect of Surface Reflection

The above equation gives the emission current in terms of the vector potential of the light wave inside the metal. To obtain the emission in terms of the incident light energy, we must find the relation between this vector potential and that of the incident wave. We can find this relation from the classical electromagnetic theory by using optical constants of the metal: n and k. The quantum theory of reflection developed by Schiff and Thomas[7] shows that the classical relations hold true for the tangential components. For the normal components the relation differs from the classical theory only in the immediate neighborhood of the surface within a thickness of the order of 10^{-8} cm. This is important for the surface effect. For the volume effect we are considering it of no importance. Let the incident wave be plane polarized, and let the subscripts i, r, and t refer to the incident, reflected, and transmitted (refracted) waves respectively.

(1) Electric vector of the incident wave parallel to the plane of incidence (x axis normal to the surface in the outward direction):

$$A_i=(\mathfrak{A}_{ix},\, -\mathfrak{A}_{ix}\cot\theta_i,\, 0)$$
$$\times\exp\frac{2\pi i\nu}{c}(x\cos\theta_i+y\sin\theta_i+ct),$$

$$A_r=(\mathfrak{A}_{rx},\, \mathfrak{A}_{rx}\cot\theta_i,\, 0)$$
$$\times\exp\frac{2\pi i\nu}{c}(-x\cos\theta_i+y\sin\theta_i+ct),$$

$$A_t=(\mathfrak{A}_{tx},\, -\mathfrak{A}_{tx}\cot\theta_t,\, 0)$$
$$\times\exp\frac{2\pi i\nu}{c}[(n-ik)(x\cos\theta_t+y\sin\theta_t)+ct].$$

The relation between θ_i and θ_t is given by

$$(n-ik)\sin\theta_t=\sin\theta_i.$$

Therefore

$$\sin\theta_t=\frac{\sin\theta_i}{n-ik};\quad \cos\theta_t=\frac{1}{n-ik}[(n-ik)^2-\sin^2\theta_i]^{\frac{1}{2}}.$$

Now curl $A=H$ and $-(1/c)(\partial A/\partial t)=E$. From the conditions of continuity for the tangential components H_z and ϵ_y, we get

$$\begin{aligned}\mathfrak{A}_{tx}&=\mathfrak{A}_i\frac{2\sin\theta_i}{(n-ik)^2+[(n-ik)^2-\sin^2\theta_i]^{\frac{1}{2}}/\cos\theta_i}=\mathfrak{A}_iK_{\parallel x},\\ \mathfrak{A}_{ty}&=-\mathfrak{A}_{tx}\cot\theta_t=-\mathfrak{A}_i\frac{2[(n-ik)^2-\sin^2\theta_i]^{\frac{1}{2}}}{(n-ik)^2+[(n-ik)^2-\sin^2\theta_i]^{\frac{1}{2}}/\cos\theta_i}=\mathfrak{A}_iK_{\parallel y}.\end{aligned} \qquad (10)$$

---

[6] This is substantially the same as Eq. (22.17), p. 457, *Handbuch der Physik*, 24/2.

[7] L. I. Schiff and L. H. Thomas, Phys. Rev. **47**, 860 (1935).

The transmitted wave in the metal is elliptically polarized since $\mathcal{A}_{tx}$ and $\mathcal{A}_{ty}$ are complex with different arguments. For the special case of normal incidence

$$K_{\parallel x}=0;\quad K_{\parallel y}=-2/(1+n-ik). \tag{11}$$

(2) Electric vector of the incident wave perpendicular to the plane of incidence:

$$A_i=(0,\,0,\,\mathcal{A}_{iz})\exp\frac{2\pi i\nu}{c}(x\cos\theta_i+y\sin\theta_i+ct),$$

$$A_r=(0,\,0,\,\mathcal{A}_{rz})\exp\frac{2\pi i\nu}{c}(-x\cos\theta_i+y\sin\theta_i+ct),$$

$$A_t=(0,\,0,\,\mathcal{A}_{tz})\exp\frac{2\pi i\nu}{c}\times[(n-ik)(x\cos\theta_t+y\sin\theta_t)+ct].$$

By the same procedure we get

$$\mathcal{A}_t=\mathcal{A}_{tz}=\mathcal{A}_i\frac{2}{1+[(n-ik)^2-\sin^2\theta_i]^{\frac{1}{2}}/\cos\theta_i}=\mathcal{A}_iK_\perp. \tag{12}$$

For the case of normal incidence

$$K_\perp=2/(1+n-ik). \tag{13}$$

The incident light energy per unit area of the surface per unit time is

$$(\pi\nu^2/2c)\cos\theta_i|\mathcal{A}_i|^2. \tag{14}$$

Substituting (10) or (12) into (9) and dividing by (14), we get the photoelectric yield, i.e., the charge emitted per unit area per unit incident energy

$$\begin{aligned} q&=\frac{4ceh}{\pi\nu^2}\left(\frac{e}{2mc}\right)^2\frac{l}{8\pi^3}\frac{1}{\cos\theta_i}\sum_g\int\int\times\frac{|K_{\parallel x}C^x_{k,\,k+2\pi g}+K_{\parallel y}C^y_{k,\,k+2\pi g}|^2}{|\nabla H|}dudv,\\ q&=\frac{4ceh}{\pi\nu^2}\left(\frac{e}{2mc}\right)^2\frac{l}{8\pi^3}\frac{|K_\perp|^2}{\cos\theta_i}\times\sum_g\int\int\frac{|C^z_{k,\,k+2\pi g}|^2}{|\nabla H|}dudv,\end{aligned} \tag{15}$$

for the two cases of electric vector parallel and perpendicular to the plane of incidence, respectively. Since the electrons excited deep inside the metal cannot be emitted because of the loss of energy by collisions with other electrons, l in these equations is an effective thickness within which excited electrons reach the surface without much loss of energy. It depends, therefore, on the collision process between electrons which is very difficult to calculate. Bethe[2] estimates the effective thickness to be of the order of 10^{-7} cm. Rudberg's experiments[8] on inelastic scattering of electrons from solids shows that electrons of 100- to 200-volts energy can penetrate several atomic layers. Compton and Rose,[9] and Goldschmidt and Dember[10] by experiments on photoelectric emission by light irradiating the back side of a thin layer, conclude that the electron mean free path in platinum is 1.08 to 2.67×10^{-7} cm. It seems then reasonable to assume that l is of the order of 10^{-7} cm.

To determine the photoelectric yield, we must know the electron energy levels for the calculation of H and the electron wave functions for the calculation of $C_{k,\,k+2\pi g}$. Such data have been obtained for a number of metals by the cellular method of Wigner and Seitz,[11] and Slater.[12] But the data have not been published in full. However, for the determination of low frequency limits for light absorption and electron emission, we need to know only electron energy levels. Knowing the energy as a function of k, we shall have the equations of the three surfaces: (5), (8), and the surface of Fermi distribution with $h\nu$ and g as parameters. The area, over which each of the integrals in the sums of (7) and (9) is to be integrated, can then be determined. For each integral (each value of g) there is a frequency below which the area and consequently the integral itself become zero. The frequency below which all integrals in (7) become zero is the long wave-length limit of light absorption; the corresponding frequency for (9) is the threshold frequency of emission. It has been shown by Wigner and Seitz,[13] and Slater[14] that except at energy discontinuities, the energy

---

[8] E. Rudberg, Phys. Rev. **50**, 138 (1936).

[9] K. T. Compton and L. W. Ross, Phys. Rev. **13**, 295 (1919).

[10] H. Goldschmidt and H. Dember, Zeits. f. tech. Physik **7**, 137 (1926).

[11] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[12] J. C. Slater, Phys. Rev. **45**, 794 (1934).

[13] E. Wigner and F. Seitz, Phys. Rev. **46**, 515 (Fig. 3), (1934).

[14] See reference 12 (Fig. 3).

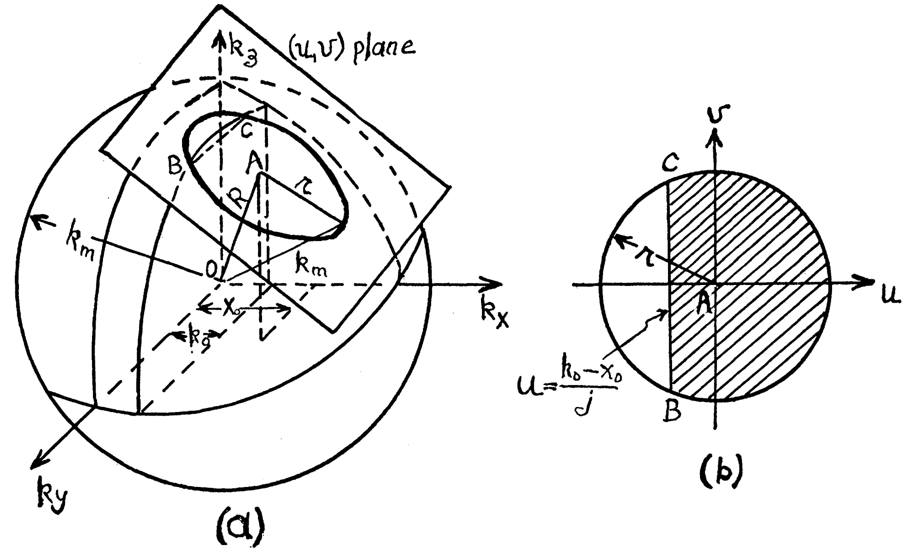

FIG. 1 (a) Geometric representation of Eqs. (17) and (18). (b) Portion of the (u, v)-plane over which the integral of Eq. (9) is to be taken.

levels of sodium are given very closely by the expression for free electrons

$$E_k=(h^2/8\pi^2m)k^2. \tag{16}$$

We shall use this approximation for the determination of threshold frequencies for sodium and potassium.

THRESHOLD FREQUENCY

Using the approximation (16) we find that Eq. (5) of the (u, v) surface becomes

$$(h^2/8\pi^2m)(\pi g^2+g\cdot k)=h\nu, \tag{17}$$

which is the equation of a plane in k-space. The surface of Fermi distribution becomes a sphere

$$k_x^2+k_y^2+k_z^2=k_m^2. \tag{18}$$

The area over which we have to integrate for (7) is the portion of (17) bounded by its intersection with (18). This is a circle with radius (Fig. 1a)

$$r=\left[k_m^2-\left(\frac{(2\pi m/h^2)h\nu-\pi g^2}{g}\right)^2\right]^{\frac{1}{2}} =(k_m^2-R^2)^{\frac{1}{2}}. \tag{19}$$

The area πr^2 is zero unless $|R|\leqslant k_m$ or

$$\pi g^2-gk_m\leqslant\frac{2\pi m}{h^2}h\nu\leqslant\pi g^2+gk_m. \tag{20}$$

This relation gives the low frequency and high frequency limits of absorption of light for the given g. The lowest of the low frequency limits for all possible values of g is the absorption limit of the metal.

For electron emission the condition (8) must be satisfied, which by the approximation (16) becomes

$$\frac{h^2}{8\pi^2m}(k_x+2\pi g_x)^2\geqslant W=E_\varphi+E_m =\frac{h^2}{8\pi^2m}(k_\varphi^2+k_m^2), \tag{21}$$

where E_φ is the work function of the metal. This can be written

$$k_x\geqslant(k_\varphi^2+k_m^2)^{\frac{1}{2}}-2\pi g_x=k_0.$$

Let point A (Fig. 1a) be the origin of coordinates in the (u, v)-plane and let the axis v be parallel to the (k_y, k_z)-plane. Then we have

$$k_x=ju+x_0,$$

where x_0 is the k_x-coordinate of point A. From (17) we have

$$x_0=Rg_x/g.$$

j is cosine of the angle between axes u and k_x

$$j=[\cos^2(0A,\,k_y)+\cos^2(0A,\,k_z)]^{\frac{1}{2}} =[(g_y/g)^2+(g_z/g)^2]^{\frac{1}{2}}.$$

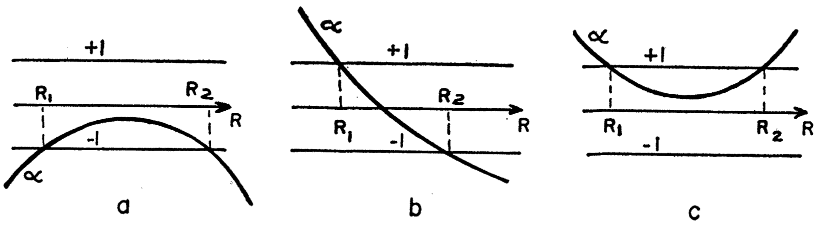

FIG. 2. Values of α:

(a) $jk_0+\frac{g_x}{g}(k_m{}^2-k_0{}^2)^{\frac{1}{2}}<0$

(b) $jk_0+\frac{g_x}{g}(k_m{}^2-k_0{}^2)^{\frac{1}{2}}>0$ and $jk_0-\frac{g_x}{g}(k_m{}^2-k_0{}^2)^{\frac{1}{2}}<0$

(c) $jk_0-\frac{g_x}{g}(k_m{}^2-k_0{}^2)^{\frac{1}{2}}>0$.

The area $\int\int dudv$ over which the integrals in (9) are to be integrated is the part of (u, v)-plane (Eq. (17)) bounded by the circle πr^2 (see (19)) and the line

$$u=(k_0-x_0)/j$$

shown by the shaded area in Fig. 1b. It is easily shown

$$\int\int dudv=\pi r^2, \quad \text{if } \alpha\leqslant -1;$$

$$\int\int dudv=r^2\{\cos^{-1}\alpha-\alpha(1-\alpha^2)^{\frac{1}{2}}\}, \quad \text{if } -1<\alpha<+1; \tag{22}$$

$$\int\int dudv=0, \quad \text{if } \alpha\geqslant +1;$$

$$\alpha=\frac{k_0-x_0}{jr}=\frac{k_0-Rg_x/g}{j(k_m{}^2-R^2)^{\frac{1}{2}}}.$$

We see that α is a function of g and ν, R being a function of ν. For each value of g we can determine the limiting frequency ν_g below which $\alpha>+1$ and $\int\int dudv=0$. The lowest of these for all possible values of g is then the threshold frequency.

To determine ν_g we shall solve the equation

$$\alpha=1, \quad \text{or} \quad (k_0-Rg_x/g)^2=j^2(k_m{}^2-R^2).$$

The two roots are

$$R=(k_0g_x/g)\pm j(k_m{}^2-k_0{}^2)^{\frac{1}{2}}.$$

We note that g_x must be positive since $g_x<0$ means decrease in the outward momentum, which certainly cannot give emission. There are then three possible cases

$$\text{(A)} \quad jk_0+\frac{g_x}{g}(k_m{}^2-k_0{}^2)^{\frac{1}{2}}<0,$$

$$\text{(B)} \quad jk_0+\frac{g_x}{g}(k_m{}^2-k_0{}^2)^{\frac{1}{2}}>0$$

and

$$jk_0-\frac{g_x}{g}(k_m{}^2-k_0{}^2)^{\frac{1}{2}}<0,$$

$$\text{(C)} \quad jk_0-\frac{g_x}{g}(k_m{}^2-k_0{}^2)^{\frac{1}{2}}>0.$$

It can be easily shown that the curves of α *versus* R for the three cases are as shown in Fig. 2. To have $\alpha<+1$, R must observe the following conditions

For case A: no limitations on R,

For case B: $R>\frac{g_x}{g}k_0-j(k_m{}^2-k_0{}^2)^{\frac{1}{2}}$,

For case C:

$$\frac{g_x}{g}k_0-j(k_m{}^2-k_0{}^2)^{\frac{1}{2}}<R<\frac{g_x}{g}k_0+j(k_m{}^2-k_0{}^2)^{\frac{1}{2}}.$$

Furthermore, if $k_0{}^2>k_m{}^2$ we have two possible cases

D: $k_0<-k_m$,

E: $k_0>k_m$.

We deduce from Fig. 2a and Fig. 2c:

For case D: α always smaller than $+1$, therefore no limitations on R.

For case E: α always larger than $+1$, therefore no emission.

TABLE I. Low frequency limit of light absorption and the threshold frequency.

Na	Emission surface	1, 0, 0	Threshold frequency	12.6×10^{14}	9.0×10^{14}			
			n_1, n_2, n_3	+1, 0, 0	+1, +1, 0	+1, −1, 0	+1, 0, +1	+1, 0, −1
		1, 1, 0	Threshold frequency	5.91×10^{14}				
			n_1, n_2, n_3	+1, +1, 0				
		1, 1, 1	Threshold frequency			7.34×10^{14}		
			n_1, n_2, n_3	+1, +1, 0	+1, 0, +1	0, +1, +1		
	Absorption limit n_1, n_2, n_3			±1, ±1, 0	3.14×10^{14} ±1, 0, ±1	0, ±1, ±1		
K	Emission surface	1, 0, 0	Threshold frequency	9.57×10^{14}	6.82×10^{14}			
			n_1, n_2, n_3	+1, 0, 0	+1, +1, 0	+1, −1, 0	+1, 0, +1	+1, 0, −1
		1, 1, 0	Threshold frequency	6.21×10^{14}				
			n_1, n_2, n_3	+1, +1, 0				
		1, 1, 1	Threshold frequency		5.69×10^{14}			
			n_1, n_2, n_3	+1, +1, 0	+1, 0, +1	0, +1, +1		
	Absorption limit				4.96×10^{14}			
	n_1, n_2, n_3			±1, ±1, 0	±1, 0, ±1	0, ±1, ±1		

Case E gives a limit for g_x, for it shows that a necessary condition for emission is $k_0 < k_m$

$$(k_m^2+k_\varphi^2)^{\frac{1}{2}}-2\pi g_x<k_m, \quad g_x>\frac{(k_m^2+k_\varphi^2)^{\frac{1}{2}}-k_m}{2\pi}.$$

This condition can also be directly deduced from (21). It gives the lower limit for g_x and confirms our previous statement that g_x must be positive. In addition to the limitations on R obtained for these different cases, we must also have $|R|<k_m$, otherwise r in (22) will be imaginary. It can be shown by combining the limitations on R that to have $\alpha<+1$ we must have

$$\begin{aligned} h\nu &> \frac{h^2}{2\pi m}(\pi g^2-gk_m) \\ &\qquad \text{if} \quad jk_0+\frac{g_x}{g}(k_m^2-k_0^2)^{\frac{1}{2}}<0, \\ h\nu &> \frac{h^2}{2\pi m}[\pi g^2+g_xk_0-((g^2-g_x^2)(k_m^2-k_0^2))^{\frac{1}{2}}] \\ &\qquad \text{if} \quad jk_0+\frac{g_x}{g}(k_m^2-k_0^2)^{\frac{1}{2}}>0. \end{aligned} \tag{23}$$

These relations give us the limiting frequency ν_g. The threshold frequency is the lowest of ν_g for all possible values of g. It can be shown that if g and g_x were continuous variables, then the minimum $h\nu_g$ is

$$(h^2/8\pi^2m)k_\varphi^2=E_\varphi,$$

which is the ordinary expression for threshold frequency. The emission due to surface effect begins at this frequency. As g and g_x can take only discrete values, the minimum ν_g will be higher than this value. This confirms the general impression that emission due to volume effect begins at a higher threshold. In general ν_g increases with g, but the lowest ν_g does not necessarily correspond to the lowest value of g. Tamm and Schubin derived by simple reasoning an expression for $\nu_{[(1/a),0,0]}$ and assumed this to be the threshold frequency for volume effect. Actually, as shown later, for body-centered cubic lattices g does not have the value $[(1/a), 0, 0]$. But even if g has such a value, the

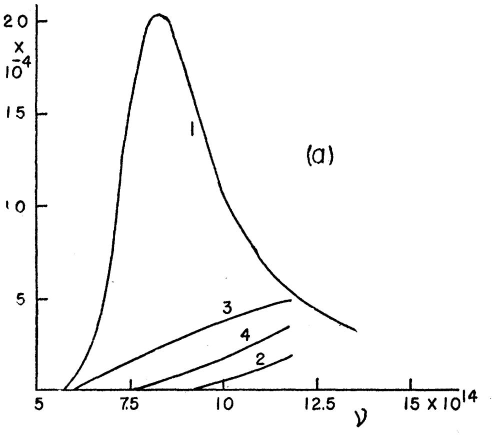

FIG. 3a. Sodium:

Curve 1. Experimental spectral distribution of photoelectric yield in coulomb/calorie.
Curve 2. $K_\nu \times 10^7$, plane (1, 0, 0).
Curve 3. $K_\nu \times 10^7$, plane (1, 1, 0).
Curve 4. $K_\nu \times 10^7$, plane (1, 1, 1).

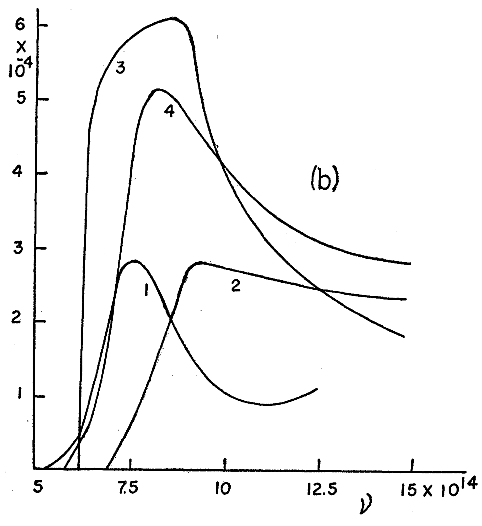

FIG. 3b. Potassium:

Curve 1. Experimental spectral distribution of photoelectric yield in coulomb-calorie.
Curve 2. $K_\nu \times 10^7$, plane (1, 0, 0).
Curve 3. $K_\nu \times 10^7$, plane (1, 1, 0).
Curve 4. $K_\nu \times 10^7$, plane (1, 1, 1).

corresponding ν_g is not the lowest both for sodium and potassium as shown in Table I; the lowest ν_g corresponds to $g=[(1/a),\ \pm(1/a),\ 0]$ and $g=[(1/a),\ 0,\ \pm(1/a)]$ which have a larger value of g.

The factor g comes from (1). For cubic lattices

$$g=\frac{1}{a}(n_1,\ n_2,\ n_3)=\frac{n}{a},$$

where n_1, n_2, and n_3 are integers, and a is the lattice constant. For body-centered and face-centered cubic lattices, the Fourier coefficients V_g can be written: $V_n=A_nS_n$, where S_n is the structure factor. Sodium and potassium have body-centered lattices for which[15]

$$S_n=1+\cos\pi(n_1+n_2+n_3).$$

Thus $S_n=0$ if $(n_1+n_2+n_3)$ is odd, and $S_n=2$ if $(n_1+n_2+n_3)$ is even. Therefore for such lattices $V_{(1,0,0)}$, $V_{(1,1,1)}$, etc., are zero, and g does not have the values $[(1/a), 0, 0]$, $[(1/a),\ (1/a),\ (1/a)]$, etc.

The maximum k of the occupied states is given by

$$k_m=(3\pi^2)^{\frac{1}{3}}(n_0/v_0)^{\frac{1}{3}}$$

where n_0 is the number of electrons per atom, and v_0 is atomic volume. For metals with one conduction electron per atom ($n_0=1$) and for body-centered cubic lattices ($v_0=a^3/2$)

$$k_m=(6\pi^2)^{\frac{1}{3}}/a.$$

The lattice constant $a=4.24\times10^{-8}$ cm for sodium and $a=5.33\times10^{-8}$ cm for potassium. For the work function we take $E_\varphi=2.29$ ev for sodium[16] and $E_\varphi=2.01$ ev for potassium.[17] From these data the low frequency limit of light absorption and the threshold frequency can be calculated from (20) and (23). These and the corresponding values of $n=g/a$ are given in Table I. The values of ν_g for the non-existent $g=[(1/a),\ 0,\ 0]$ is also given. The threshold frequency depends upon what lattice plane is the surface of emission, since the value of g_x depends upon the direction of x (direction normal to the surface of emission). The table gives threshold frequency for three different lattice planes. For sodium the plane (1, 1, 0) gives the lowest threshold 5.91×10^{14}; whereas for potassium, the plane (1, 1, 1) gives the lowest threshold 5.69×10^{14}. These are higher than the corresponding ordinary thresholds of emission E_φ/h (5.53×10^{14} for sodium and 4.84×10^{14} for potassium). The low frequency limit of light

---

[15] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys*, p. 158.

[16] M. W. Mann, Jr. and L. A. DuBridge, Phys. Rev. **51**, 120 (1937).

[17] R. Suhrmann and H. Theissing, Zeits. f. Physik **52**, 453 (1928).

absorption is 3.14×10^{14} for sodium and 4.96×10^{14} for potassium. Although experiments do not show strong absorption for these metals in the visible and ultraviolet regions, but, as pointed out by Kronig,[18] the "conductivity" ($nk\nu$), characterizing the absorption, computed from experimental data is 10 times larger than the value calculated theoretically without taking into account the photoelectric absorption. So, although light is weakly absorbed in these regions, it should be almost entirely due to such absorption.

APPROXIMATE ESTIMATION OF THE PHOTOELECTRIC YIELD

Without data on electron wave function, the photoelectric yield cannot be calculated. We shall attempt to estimate approximately its order of magnitude. Using (16) we get from (5)

$$\nabla H=\nabla\left[\frac{h^2}{2\pi m}(\pi g^2+g\cdot k)-h\nu\right]$$

$$=\frac{h^2}{2\pi m}\nabla(g\cdot k)=\frac{h^2}{2\pi m}g.$$

Substituting this into (15) and writing $\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}$ for the average value, we get for normal incidence

$$q=1.395\times 10^{-2}\left\{\frac{4ceh}{\pi\nu^2}\left(\frac{e}{2mc}\right)^2\frac{1}{8\pi^3}\frac{2\pi m}{h^2}\right.$$

$$\left.\times\left|\frac{2}{1+n-ik}\right|^2\sum_g\frac{1}{g}\int\int dudv\right\}$$

$$\times l\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}\frac{\text{coulomb}}{\text{calorie}}$$

$$=K_\nu l\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}\frac{\text{coulomb}}{\text{calorie}} \qquad (24)$$

all factors being in e.s.u. The integrals $\int\int dudv$ can be calculated from Eq. (22). From the data of Ives and Briggs[19] for n and k, the factor K_ν is calculated and shown in Fig. 3. The value of $\int\int dudv$ depends upon what lattice plane is the emission surface; K_ν is calculated for three different planes, i.e., (1, 0, 0), (1, 1, 0), and (1, 1, 1).

TABLE II.

		Sodium							
ν	10^{14}	4.96	6.0	7.0	9.0	11.0	13.0	15.0	
R_ν	10^{-14}	0	0.666	0.889	1.583	1.597	1.081	0.881	
		Potassium							
ν	10^{14}	3.14	5.2	6.0	7.0	8.0	9.0	11.0	11.82
R_ν	10^{-14}	0	0.083	0.274	0.417	0.624	0.842	1.80	2.61

The rate of consumption of energy per unit volume by the excitation of electrons is

$$P_e=(N/\Omega)h\nu.$$

The number of excited electrons per unit time N is given by (7)

$$P_e=\left\{h\nu\frac{2h}{8\pi^3}\left(\frac{e}{2mc}\right)^2\frac{2\pi m}{h^2}\sum_g\frac{1}{g}\int\int dudv\right\}$$

$$\times\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}|\mathcal{A}|^2. \qquad (25)$$

TABLE III.

r_s	3.21	3.33	3.62	3.88
$E_{2\pi g}-E_0$	0.64	0.60	0.50	0.43
$C_{0,2\pi g}$	0.2402	0.2214	0.1720	0.1407
$E_{2\pi g}-E_0$	2.27	2.10	1.79	1.54
$C_{0,2\pi g}$	0.2718	0.2565	0.2317	0.2142
$E_{2\pi g}-E_0$	4.84	4.55	3.95	3.47
$C_{0,2\pi g}$	0.2045	0.1822	0.1568	0.1513

The rate of loss of energy per unit volume by the light wave is

$$P_l=\tfrac{1}{2}nk\nu|\epsilon|^2=\frac{2\pi^2}{c^2}nk\nu^3|\mathcal{A}|^2. \qquad (26)$$

The ratio is

$$\frac{P_e}{P_l}=\left[\frac{c^2}{2\pi^2}\frac{2h^2}{8\pi^3}\left(\frac{e}{2mc}\right)^2\frac{2\pi m}{h^2}\sum_g\frac{1}{g}\int\int dudv\right]\frac{1}{nk\nu^2}$$

$$\times\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}=R_\nu\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}. \qquad (27)$$

The integrals $\int\int dudv$ can be calculated by using (19). As pointed out above, the energy loss of the light wave is almost entirely due to photoelectric absorption, so the ratio P_e/P_l should be nearly equal to one. Table II gives calculated values of R_ν. We see that to make $P_e/P_l\approx 1$ the factor $\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}$ should be $\sim 10^{14}$.

Although the factor $\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}$ is not the same in (27) and (24), as it is not averaged over the same area in the two cases, its magnitude

---

[18] R. de L. Kronig, Nature **133**, 211 (1934).

[19] H. E. Ives and H. B. Briggs, J. Opt. Soc. Am. **26**, 238 (1936); **27**, 181 (1937).

will not be very different. We have stated that l should be $\sim 10^{-7}$ cm, so the product $l\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}\sim 10^7$. From curves K_ν in Fig. 3, we see that the photoelectric yield will be between 10^{-4} to 10^{-3} coulomb/calorie. The experimental values of absolute photoelectric yield for these metals are not very reliable because of the difficulty of obtaining perfectly clean surfaces for these very active metals. In Fig. 3 the curves of Hill[20] (computed from data of Mann and DuBridge[16]) for sodium, and Suhrmann and Theissing[17] for potassium are reproduced. It is seen that our estimated photoelectric yield is comparable with the experimental values in order of magnitude. It may perhaps be too small for sodium and too large for potassium. Anyway, for both metals the photoelectric yield calculated from surface effect is the same in order of magnitude as our estimated values.[21] As to the shape of spectral distribution curves, it cannot be predicted in our case without detailed knowledge of electron wave functions, since $\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}$ is a function of frequency and the curves K_ν do not, therefore, represent the shapes of the distribution curves. Furthermore, the metal is usually not a single crystal, and the surface is not a single plane; therefore the spectral distribution curve should be a combination of those for different planes.

Seitz gives for lithium the values of

$$C_{0,2\pi g}=\int\psi^*_{2\pi g}\frac{\partial\psi_0}{\partial x}d\tau$$

for several values of g. In Hartree's units the results are[22] those shown in Table III. We see that the larger the radius of atomic spheres r_s, or rather the larger the part of the atomic volume in which ψ is constant, the smaller becomes $C_{0,2\pi g}$. The radius of atomic spheres for sodium is 3.9 (Hartree's unit), and the region around the nucleus, within which the wave function is not constant, is about the same as for lithium.[23] Therefore $C_{0,2\pi g}$ should be 0.1 to 0.2 in Hartree's units. The same is probably true also for potassium which has still larger radius of atomic spheres, $r_s=4.93$. We have estimated

$$\begin{aligned}\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}&\backsim 10^{14}\text{ absolute units}\\&=0.0073\text{ Hartree's units}\\(\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}})^{\frac{1}{2}}&\sim 0.085\text{ Hartree's units.}\end{aligned}$$

Although $C_{0,2\pi g}$ and $(\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}})^{\frac{1}{2}}$ are not the same, we may judge from this that our estimated value is quite reasonable. It is satisfying that our equation of absorption (25) with a reasonable value for $\langle|C_{k,k+2\pi g}|^2\rangle_{\text{Av}}$ should agree with the absorption given by experimental values of n and k $[(P_e/P_l)\eqsim 1]$.

CONCLUSION

Although emission due to volume effect does begin at a higher frequency, at least for sodium and potassium it comes in over most of the region for which spectral distribution has been investigated experimentally, long before the maximum in the distribution curve is reached. The estimated order of magnitude of photoelectric yield is the same as that calculated from surface effect and is comparable with that observed experimentally. Therefore the volume effect cannot justifiably be neglected in the theory of photoelectric emission except for the immediate neighborhood of the threshold frequency. It is then worth the labor to calculate accurately the spectral distribution curve by use of the electron wave functions. It would also be interesting to calculate accurately the energy loss due to photoelectric absorption to compare with the light absorption computed from experimental values of n and k.

Recently Cashman and Bassoe[24] working with barium, which has more stable surface than the alkali metals, have observed an abrupt second rise in the spectral distribution curve which they attribute to the onset of the volume effect. Unfortunately, the free electron approximation for energy cannot be applied to this metal with justification, and we cannot calculate the threshold frequency by the same method used here for sodium and potassium. We have to wait for the solution of electron energy levels for this metal.

---

[20] A. G. Hill, Phys. Rev. **53**, 184 (Fig. 8), (1938).

[21] R. E. B. Makinson, Proc. Roy. Soc. **A162**, 367 (1937); R. J. Maurer, Phys. Rev. **57**, 653 (1940).

[22] F. Seitz, Phys. Rev. **47**, 404 (1935), Table III.

[23] Cf. reference 13, Fig. 1, and reference 22, Fig. 3.

[24] J. Cashman and E. Bassoe, Phys. Rev. **55**, 63 (1939).