DETERMINATION OF FLUORESCENCE YIELD BY MEASURING THE X-RAY PHOTOELECTRIC EFFECT IN A MASSIVE CATHODE

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Different groups of photoelectrons from the x-ray photoelectric effect in a massive cathode are analyzed. It is shown that with variation of the x-ray wavelength the contributions of different photoelectron groups change; at the K edge the contribution of one electron group to external emission vanishes, resulting in a jump of the quantum yield. It is also shown that the experimental jump of the quantum yield is related directly to the Auger yield and that the Auger yield and fluorescence yield can be calculated from a measurement of the jump of the photoelectric quantum yield. The derived formulas are verified for Cr. The Auger yield based on photoemission data is shown to agree satisfactorily with the mean value of other authors. The photoelectric effect is used to determine the fluorescence yields of Ti, V, and Mn; only a few earlier measurements are known. The atomic number range in the periodic table where the photoelectric effect can be used successfully is indicated.

INTRODUCTION

TRANSITIONS to lower excited levels can occur in atoms excited to the K level with emission of either a quantum (radiative transition) or an Auger electron (nonradiative transition).\[2\] The ratio of the number of radiative transitions to the total number of excitations of the i-th level is called the fluorescence yield, while the ratio of the number of nonradiative transitions to the total number of excitations is called the Auger yield. Denoting the fluorescence yield by \(w_v\) and the Auger yield by \(w_e\), it follows by definition that

\[ w_v + w_e = 1. \]

The values of \(w_v\) and \(w_e\) for different elements and different theories is of considerable interest for both theory and applications. Knowledge of \(w_v\) is of practical interest in connection with the development of methods for x-ray spectrum analysis. The theoretical interest of \(w_v\) results from the fact that the probabilities of Auger transitions and radiative transitions are directly related to the widths of x-ray levels. Nevertheless, at the present time \(w_v\) and \(w_e\) are unknown for many elements, since their experimental determination by the Compton method\[6\] is extremely complicated, while the method involving K capture\[3\] can be employed only when a suitable radioactive isotope exists. It is therefore of interest to examine the possibility of determining \(w_v\) by other methods, particularly by means of the photoelectric effect.

1. BASIS OF THE METHOD

In our earlier work\[7\] on the mechanism of the x-ray photoelectric effect it was shown that the quantum yield \(\kappa\) of a massive cathode is given by

\[ \kappa = 1 - R(\theta) \left[ \frac{P_1}{T + \mu_1 \alpha_1 \sin \theta} + \frac{P_2}{T + \mu_2 \alpha_2 \sin \theta} + \ldots \right], \]

(1)

where \(R(\theta)\) is the reflection coefficient of x rays impinging on the photocathode at the angle \(\theta\) to the surface; \(\mu\) is the linear absorption coefficient of x rays in the photocathode material; \(P_1, P_2, \ldots\) are the probabilities that different groups of photoelectrons will be produced through the absorption of a single quantum; \(\alpha_1, \alpha_2, \ldots\) are the linear attenuation coefficients of electron flux for different energies.

Since each coefficient \(\alpha\) is inversely proportional to the square of electron energy\[8\] the larger part of the sum within square brackets in (1) will come from terms for electrons of relatively high energies. In the case of the photoelectric effect induced by radiation capable of ionizing the K shell of photocathode atoms, three groups of these electrons appear:

1) Photoelectrons are ejected from the K shell with energy \(h\nu - K\), where \(h\) is Planck's constant,
\( \nu \) is the x-ray frequency, and \( K \) is the K-shell ionization energy.

According to Stobbe's theory[2] the probability \( P_1 \) of the appearance of these electrons is given approximately by \((SK - 1)/SK\), where \( SK \) is the so-called K jump value for absorption, which we shall denote simply by \( S \). The accuracy of this definition of the probability increases as the wavelength approaches the K absorption edge. Since we shall be interested in the photoelectric effect near the K edge we shall regard this expression for the probability as accurate.

2) Auger electrons appear when ionization of the K shell in the photocathode is followed by transitions to lower levels. The most probable energy of these electrons is \( K_Z - [(L_I)Z + (L_{II})Z + 1] \) = \( K_Z - 2(L_I)Z \), where \( L_I \) and \( L_{II} \) denote the corresponding energies and the subscripts \( Z \) and \( Z + 1 \) denote atomic numbers. The probability of Auger electrons of this kind is obviously \( P_2 = (S - 1)_{\omega_0}/S \).

3) Photoelectrons ejected from the L and M shells will possess the higher energies \( h\nu - L \) and \( h\nu - M \) etc. The energy difference (of the order \( L - M \)) is small compared with the energies themselves (which for \( h\nu \geq K \) will be at least \( K - L \)), and these electrons can be regarded as monoenergetic in first approximation. The energy of this group will be \( h\nu - L \), where \( L \) is the mean energy of the L shell, computed by weighting each L shell, as well as the M and N subshells. From a rigorous point of view \( L \) should depend on the incident wavelength, since the relative probabilities or weighting coefficients used in calculating \( L \) depend on the wavelength. However, we shall be interested in the narrow spectrum region adjacent to the K absorption edge; therefore in determining the energy of this electron group we shall have to compute \( L \) for radiation at the K edge.

The probability that an electron of this group will be emitted is determined by the fraction of x-ray quanta absorbed in all shells except the K shell; this is \( P_3 = 1/S \). Additional photoelectrons (not included in the given groups) will result from K fluorescence partially absorbed in the photocathode. The energy of these electrons will be given by \((K - L)Z - L_Z \), which approximates the energy of the second group.

For ease in calculating the probability of these last electrons the following two simplifying assumptions are made:

1) Figure 1 shows the portion of the photocathode facing the window of the photoemission detector. Emission from the hatched region of the photocathode surface is registered. Two layers are represented under the photocathode surface. Emission from the layer (of thickness \( \text{d}X_0 \)) at the depth \( X_0 \approx 1/\alpha \) can enter the vacuum. Electrons coming from this layer are registered only if they pass through the hatched region of the surface. Therefore in the layer \( \text{d}X_0 \) we must distinguish the effective region where the photoelectric effect is important for our experiment (the hatched region in Fig. 1). The second layer (of thickness \( \text{d}X \)) at the depth \( X \approx 1/\alpha \) can enter the primary fluorescence-inducing radiation. It is essential to note that only the region of the \( \text{d}X \) layer to which the primary x rays penetrate will fluoresce. This region is hatched in Fig. 1. The calculation of the probability that an electron will be produced by fluorescence is simplified by assuming that the area of the hatched region of \( \text{d}X_0 \) is much larger than the region of \( \text{d}X \) in the path of the x-ray beam. This assumption is required so that in calculating the ionization induced in \( \text{d}X_0 \) by fluorescence from \( \text{d}X \) we can take into account the fluorescence propagating in all directions in a half-space.

With regard to the technique for measuring photoemission described in [10] the foregoing assumption is realistic, since the effective window of the vacuum electron multiplier has an area of the order 10 mm², whereas the cross-sectional area of the primary beam is of the order of tenths of one mm². With these areas and under the condition that the layers are separated by less than \( X \approx 1/\mu \approx 10^{-2} \) mm, all directions in the half-space can be taken into account.

2) For a rigorous calculation of the probability of fluorescence-induced electron emission we must, of course, take account of ionization in \( \text{d}X_0 \).
induced by fluorescence from all layers of the photocathode. However, the fraction of fluorescing layers lying above dX_q is incomparably smaller than the fraction of layers lying below dX_q, since 1/\mu \gg 1/\alpha (1/\alpha = 10^{-4} \text{ mm}). Moreover, most of the external photoemission will come from dX_q layers for which X_q < 1/\alpha, in which case the fraction of fluorescing layers lying above dX_q will be negligible. To simplify the calculation we can therefore neglect fluorescence of layers lying above dX_q, and in calculating the total effect we can integrate over X from X_q to \infty instead of from 0 to \infty.

In calculating the required probability we assume that the photocathode is struck by N x-ray quanta at the angle \theta to the surface (Fig. 2). The layer dX at depth X absorbs

\[ dN = N[1-R(\theta)]e^{-\mu X \sin \theta} \frac{dX}{\sin \theta} \]  

quanta which excite (S - 1)dN/S atoms in the dX layer to the K level. If the fluorescence yield of the photocathode material is \psi f = 1 - \psi_e then the number of K-fluorescence quanta originating in the layer dX is \( dF = [(S - 1)/S] (1 - \psi_e) dN \). The flux in directions at the angle \psi to the normal on the photocathode surface will contain

\[ dF = [(S - 1)/S] (1 - \psi_e) dN \sin \psi \frac{d\psi}{2} \]

quanta. Before reaching the layer dX_q this flux will be attenuated by the factor \( \exp \left\{ -\mu (X - X_q)/S \cos \psi \right\} \), so that the number of fluorescence quanta emitted from dX at the angle \psi to the normal and absorbed in dX_q is

\[ \frac{dF}{dX_q} = \frac{S}{\mu S \cos \psi} \left( \psi_e - \frac{1}{2} \psi_e \cos \psi \right) \left( 1 - \frac{\mu (X - X_q)}{S \cos \psi} \right) \]  

Since each absorbed quantum produces an electron with energy (K - L) - \lambda, d\lambda electrons will appear in the layer; this equals exactly the number of absorbed quanta. When dN in (3) is replaced by (2), d\lambda can be put into a form suitable for integration over X and \psi. This substitution gives

\[ d\lambda = \frac{S - 1 - \psi_e}{S} N \left[ 1 - R(\theta) \right] \frac{\mu X_q}{\sin \theta} \exp \left\{ \frac{\mu X_q}{S \cos \theta} \right\} dX_q \times \frac{d\psi}{d\theta} \left( \psi_e - \frac{1}{2} \psi_e \cos \psi \right) \]  

Integrating (4) over X from X_q to \infty, and then over \psi from 0 to \pi/2, we obtain

\[ d\lambda = \frac{S - 1 - \psi_e}{S} N \left[ 1 - R(\theta) \right] \frac{\mu X_q}{\sin \theta} \exp \left\{ \frac{\mu X_q}{S \cos \theta} \right\} \]  

\[ \times \frac{1}{2} \psi_e \cos \psi \left( 1 + \frac{\psi_e}{\sin \theta} \right) \ln \left( 1 + \frac{S}{\sin \theta} \right). \]

In accordance with (2), the expression

\[ N(1 - R(\theta)) \exp \left\{ -\mu X_q / \sin \theta \right\} (\mu / \sin \theta) dX_q \]

is replaced by dN_q, representing the number of quanta absorbed in dX_q; we thus obtain

\[ dN_q = \frac{S - 1 - \psi_e}{S} \frac{1 - \psi_e}{2} \sin \theta \ln \left( 1 + \frac{S}{\sin \theta} \right) dN_q. \]  

Dividing (5) by dN_q, we obtain the probability that fluorescence will produce an electron in dX_q when a single quantum is absorbed. This probability, which can be added to the probabilities for the electrons of the aforementioned three groups, is

\[ P_a = \frac{S - 1 - \psi_e}{S} \frac{1 - \psi_e}{2} \sin \theta \ln \left( 1 + \frac{S}{\sin \theta} \right). \]  

As already mentioned, the energy of fluorescence electrons is close to that of the second group. Also, the conditions for the production of fluorescence electrons are the same as for the Auger electrons comprising the second group. Both groups appear when photocathode atoms are excited to the K level, i.e., when the incident wavelength is smaller than the K edge. It is therefore feasible to include the fluorescence electrons in the second group, with the combined probability

\[ P_a = P_a + P_n \]

\[ = \frac{S - 1 - \psi_e}{S} \left[ \psi_e + \frac{1 - \psi_e}{2S \sin \theta} \ln \left( 1 + \frac{S}{\sin \theta} \right) \right]. \]

This formula enables us to calculate the relative role of fluorescence electrons in the combined second group. We observe, first of all, that these electrons will play a role of decreasing importance as \psi_e and S increase. Secondly, this role depends on the angle of incidence of the primary radiation. Since the product \sin \theta ln (1 + S/\sin \theta) decreases as \theta decreases, the relative contribution of fluorescence electrons, whose probability is computed approximately, will decrease when measurements are obtained at small angles \theta. Thus at \theta = 20° with a Zn photocathode (S = 7.9, \psi_e = 0.55) a calculation based on (7) indicates that the second group consists 97.7% of Auger electrons and only 2.3% of fluorescence electrons.

The foregoing three groups of electrons correspond to the three principal terms in (1). These terms are sufficient if all remaining terms are so small that their omission results in an error considerably smaller than our \sim 5\% experimental error. To estimate the relative contribution of additional terms in (1) we shall consider the group of electrons produced when L excitation disappears. This group will be the most important of all groups hitherto neglected with respect to both the number and energy of electrons.
L excitation can result from the absorption of radiation, from transitions of both kinds in K-excited atoms, and through the absorption of K fluorescence by L-shell electrons. The disappearance of L excitation will be predominantly nonradiative with the ejection of Auger electrons having energy approximately equal to L - 2M. L-shell fluorescence absorbed by M-shell electrons produces electrons with this energy. To avoid underestimating the contribution of the dropped terms we shall assume that the probability of the appearance of these electrons per single quantum absorption in the layer \( dx \) is equal to unity. Of course, this amounts to an overestimation of the role of this electron group and of the corresponding fourth term in (1). However, when we compare the coefficient \( 1/\alpha_4 \) of this term with the coefficient \( 1/\alpha_2 \) of the term for the second group it becomes clear that the contribution of the fourth term, which is the largest of the neglected terms in (1), will be negligible. Indeed, assuming that \( 1/\alpha \) is proportional to the square of the energy and using the crudest approximation to calculate the energy levels \( E = k/n^2 \), where \( k \) is a constant, and the principal quantum number \( n \) is 1, 2, 3, ... for the K, L, M, ... levels), it is easily computed that \( K - 2L \) is 18 times larger than \( L - 2M \), and that \( 1/\alpha_2 \) is 324 times larger than \( 1/\alpha_4 \).

We have thus found that the most important of the neglected terms in (1) is that associated with electrons having energy \( L - 2M \), and that all other terms can be neglected.

The foregoing estimate enables us to simplify (1) by retaining only the first three terms. At the same time we can neglect \( \mu/\alpha \sin \theta \) compared with unity, writing the quantum yield of the photoelectric effect as

\[
\kappa = \frac{(1 - R(\theta)) \mu}{2 \sin \theta} \left( S - \frac{1}{3} \right) + \frac{S - 1}{S} \left[ \omega + \frac{1 - \omega}{2S} \sin \theta \ln \left( 1 + \frac{S}{\sin \theta} \right) \frac{1}{\alpha_2} + \frac{1}{S \alpha_2} \right].
\]

Since \( \mu, \alpha_2, \) and \( \alpha_3 \) vary along the spectrum, it is seen from (8) that \( \kappa \) is an implicit function of the wavelength \( \lambda \).

Special interest attaches to the portion of the dependence of \( \kappa \) on \( \lambda \) that is associated with the spectral variation of \( \alpha_2 \) and \( \alpha_3 \). Thus, as \( \lambda \) increases from small wavelengths toward the K edge, \( \alpha_2 \) will increase and reduce the relative contribution of the first term. For values of \( \lambda \) close to the K edge the energy of first-group electrons becomes very small and \( 1/\alpha_4 \) becomes so large that the first term in (8) can be neglected.

In the immediate vicinity of the absorption jump on its short-wavelength side the photoelectric effect is determined mainly by electrons of the second group and only to a small extent by the third group, which is generated with relatively small probability. The jump of the quantum yield upon passing through the K edge results from the disappearance of the second group. As valid formulas close to the K edge we have

\[
\kappa (\lambda_{K-\delta}) = \left[ \frac{1 - R(\theta)}{2 \sin \theta} \right] \left( S - \frac{1}{3} \right) \left[ \omega + \frac{1 - \omega}{2S} \sin \theta \ln \left( 1 + \frac{S}{\sin \theta} \right) \frac{1}{\alpha_2} + \frac{1}{S \alpha_2} \right] + \frac{1}{S \alpha_2},
\]

\[\kappa (\lambda_{K+\delta}) = (1 - R(\theta)) \mu/2 \sin \theta \cdot \delta \alpha_2. \]

where \( \delta \) a small change of wavelength.

If the quantum yield jump is represented by the ratio

\[\kappa (\lambda_{K-\delta}) / \kappa (\lambda_{K+\delta}) = \sigma,\]

we have the equation

\[
\sigma = \left[ \frac{S - 1}{\alpha_2 S} \left( \omega + \frac{1 - \omega}{2S} \sin \theta \ln \left( 1 + \frac{S}{\sin \theta} \right) \frac{1}{\alpha_2} + \frac{1}{S \alpha_2} \right) \right] \frac{1}{\alpha_3}. \]

From this we easily determine

\[
\omega = \left[ \frac{\alpha_2 S - 1}{\alpha_2 S - 1} \frac{1}{\alpha_2} \right] \frac{\sin \theta}{2S} \ln \left( 1 + \frac{1}{S \sin \theta} \right) \left[ \frac{1 - \sin \theta}{2S} \ln \left( 1 + \frac{S}{\sin \theta} \right) \right]. \]

This last equation contains the ratio of the linear attenuation coefficients of electron fluxes with the energies \( K - 2L \) (\( \alpha_2 \) for the second group) and \( h\nu - L \approx K - L \) (\( \alpha_3 \) for the third group). In this case we can replace \( h\nu \) with \( K \), since in determining \( \sigma \) we use the values of \( \kappa \) at the absorption jump, where \( h\nu = K \).

It is clear from that the experimental determination of the coefficients \( \alpha \) is laborious; therefore, on the basis of the relation \( \alpha = C e^2 \), we replace the ratio \( \alpha_2/\alpha_3 \) with \( (K - L)^2/(K - 2L)^2 \).

To calculate \( \omega \) we then have to determine only \( \sigma \), since \( S \), if unknown, can be computed from Jönsson's rule.

2. EXPERIMENT

Our technique for determining jumps \( \sigma \) of the quantum yield has been described in [13]. However, in that earlier work we used ground and polished photocathodes. It was found that the properties of cathodes prepared in this manner are not reproducible, evidently as a result of indeterminate structure and chemical composition near the surface. It is found that a layer \( \sim 10^3 \text{Å} \) thick accounts for the magnitude of the
quantum yield, a special part being played by the surface layer. It has been shown experimentally that reproducible results are obtained only from photocathodes having a surface layer prepared by vacuum evaporation. Very suitable photocathodes are made by vacuum deposition of layers a few thousand Å thick on polished flat glass slabs. For the investigation of a dielectric it was found useful to have a vacuum-deposited Al layer on the glass.

When the evaporation takes place in a vacuum of the order $10^{-5}$ mm Hg we obtain fully satisfactory reproducibility of the properties of photocathodes made from materials that are stable against atmospheric action. For the investigation of a dielectric it was found useful to have a vacuum-deposited Al layer on the glass.

By measuring the quantum yield from a few Cr specimens of different thicknesses and employing the technique described by us in [14], we determined $\alpha$ before and after the jump. Whereas the values of $\alpha$ obtained for $\lambda \geq \lambda_K$ correspond to monoenergetic electrons of the third group and give us the value of $\alpha_3$, the value of $\alpha$ for $\lambda \leq \lambda_K$ gives us an effective value $\alpha_{\text{eff}}$ for the flux consisting of electrons of the second and third groups.

In accordance with the relations on which the determination of $\alpha$ is based, our value $\alpha_{\text{eff}}$ is related to $\alpha_2$ and $\alpha_3$ by

$$\frac{S + 1}{S} \left( \frac{1}{w_e} + \frac{1}{2S} \sin \theta \ln \left( 1 + \frac{S}{\sin \theta} \right) \right) \frac{1}{\alpha_2} + \frac{1}{\alpha_3} = \frac{1}{\alpha_{\text{eff}}}.$$  \hfill (12)

From the knowledge of $w_e$ for Cr and the experimental values of $\alpha_2$ and $\alpha_{\text{eff}}$ we calculated $\alpha_2$ from (12), obtaining $\alpha_2 = 1.85 \times 10^5$ cm and $\alpha_3 = 1.40 \times 10^6$ cm, which give the ratio $\alpha_2/\alpha_3 = 1.32$. The calculation of $(K-L)^2/(K-2L_1)^2$ from tables in [14] yields 1.31, in quite accurate agreement with $\alpha_2/\alpha_3$. These measurements and calculations have convinced us that we can hereafter avoid laborious experiments for the measurement of $\alpha_2$ and $\alpha_3$ and can determine $\alpha_2/\alpha_3$ from the energies of the corresponding groups.

To determine the quantum yield jump $\sigma$ we measured $\kappa$ for Cr irradiated with ten lines (the $K_\alpha$ lines of Zn, Cu, Ni, Co, Fe, Mn, Cr, V, Ti, and Ca); the results are plotted in the graph of $\log_{10} \kappa$ vs $\log_{10} \lambda$ shown in Fig. 3, where the two rectilinear branches are extrapolated up to $\log_{10} \lambda$ of the K edge. By measuring the ordinate difference of the two branches at the point $\log_{10} \lambda$ of the K edge, one easily determines $\log_{10} \sigma$, from which $\sigma$ is obtained. This procedure for obtaining $\sigma$ insures incomparably greater accuracy than that for determining the individual values of $\kappa$. The plotting of these straight lines automatically excludes random errors of the individual measurements, and the effect of a systematic error in determining $\kappa$ is reduced because $\sigma$ is a quantum yield ratio.

Having obtained $\sigma$ in the foregoing manner for several specimens prepared at different times, we determined the possible error from the range of $\sigma$, and used the mean of $\sigma$ as its final value. For a Cr photocathode we thus have $\sigma = 5.55 \pm 0.08$.

The computation of $w_e$ required data for $S$, which can unfortunately not be found in the literature, so that we were forced to use Jönsson's method of calculating $S$. This was done for the four elements Ti, V, Cr, and Mn. By plotting the experimental dependence of $S$ on Z from the literature (the circles and curve in Fig. 4) together with the values of $S$ for Ti, V, Cr, and Mn calculated from Jönsson's rule (the crosses in Fig. 4), we easily find that this calculation gives a gener-
ally correct form of the dependence of $S$ on $Z$ but undervalues $S$. The question as to whether the calculated value of $S$ for Cr or that obtained by interpolating experimental results (using Fig. 4) should be used in computing $w_\nu$ was decided in favor of the latter, giving the value 8.9.

A calculation based on (11) furnished the result $w_\nu = 0.74$, which coincides with the mean value obtained by other methods. This agreement indicates that the proposed method is suitable for uninvestigated elements. We applied the method to Ti, V, and Mn, for which the fluorescence yields are not known reliably. The table gives the results obtained from this work.

The graph of $w_\nu$ vs $Z$ in Fig. 5 shows our results (open circles) and the average values obtained by other methods ([2], p. 172) for neighboring elements (filled circles); a single curve fits both sets of values. Other determinations [1,3-5] of $w_\nu$ for Ti, V, Cr, and Mn lie off this curve.

We have not reached the limit of accuracy in the present work. An improvement of our technique for measuring the quantum yield will enable us to reduce the random errors affecting $\kappa$, and thus enhance the accuracy of $\sigma$ and $w_\nu$. The values obtained for $w_\nu$ will be more reliable if experimentally measured values of $S$ are used in the calculation.

In evaluating the proposed method of determining $w_\nu$ it must be pointed out that the reliability of the method will increase with $w_\nu$, i.e., with decreasing atomic number. Direct measurements are difficult in this region, since the fluorescent emission then lies in the soft and ultra-soft x-ray spectrum.

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