Mechanism of Exciton-Enhanced Photoelectric Emission in Alkali Halides

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(Received November 15, 1950)

A theoretical interpretation is made of the photoelectric yield from RbI as observed by Apker and Taft. The mechanism used is the following: (1) In the neighborhood of the first peak in the optical absorption, excitons produced in the crystal diffuse to F-centers and eject electrons from them. (2) The electrons diffuse to the surface and appear as external photo-electrons. Competing with (1) are other processes of destruction of excitons. It is found necessary to suppose that these are localized near the surface to form a dead layer either because of preferential destruction there or a sparsity of F-centers needed for (1). In (2) electrons gradually lose energy to the lattice so that probability of escape through the surface decreases with increasing depth of origin. Combination of these two effects gives photoelectric yield first rising then falling with increasing absorption coefficient in agreement with observation. Energy distribution of emitted electrons is calculated and compared with experiment.

I. INTRODUCTION

THE photoelectric yield from films of RbI containing F-centers both at 300°K and 85°K has been measured by Apker and Taft.[1] In the region of the first maximum in the optical absorption, they find a remarkable difference in the form of the photoelectric emission at the two temperatures. At the higher temperature, the emission has a single peak corresponding closely to the optical peak. At the lower temperature, the emission shows a double peak, the valley between coinciding with the peak in the optical absorption. Apker and Taft explain this phenomenon in the following way. The peak optical absorption is some 70 percent greater at 85°K than at 300°K. Suppose now that the photoelectric yield first rises with increasing absorption coefficient, reaches a maximum, and then falls. The observed behavior will follow if the absorption at which the yield is a maximum lies between the peak absorptions at 300°K and 85°K. It is the purpose of the present paper to give a more quantitative account of this effect.

II. FORMATION AND DESTRUCTION OF EXCITONS

Following Apker and Taft,[2] we suppose that electrons ejected by absorption in the first optical absorption peak are the result of a secondary process. An exciton produced by the primary absorption diffuses to an F-center in the crystal, where it ejects the electron from the center and is simultaneously destroyed.[3] The photoelectric yield consists of those electrons that are able to escape through the surface from their point of origin in the crystal.

One can represent the yield in electrons per quantum as the integral of a product

$$Y=\int_0^\infty S(z)P(z)dz, \tag{1}$$

in which S is the number of electrons per unit depth produced at depth z by a single incident quantum and P is the probability of escape from this depth. It is presumed that $P(z)$ is a decreasing function of z. A simple assumption would be to let

$$S(z)=\alpha e^{-\alpha z}, \tag{2}$$

where α is the optical absorption coefficient; i.e., to suppose that the generation of electrons is proportional to the destruction of light quanta at each point. However, this immediately gives a yield Y which, contrary to the experimental result, always increases with α. In order to get a maximum in Y with respect to α, it is necessary to reduce S compared to (2) at small z; in other words, to reduce the production of electrons near the surface. The following mechanisms might be expected to contribute to this result.

(A) Excitons may be preferentially destroyed at the crystal surface. Fano[4] has used this hypothesis to explain the low efficiency of phosphors under bombardment by electrons of low energy.

(B) Excitons may experience a force urging them toward the surface. This would make (A) more effective than with diffusion alone. In principle, one should expect a dipole image force and a force due to distortion of the crystal near the surface.

(C) The density of F-centers at the surface may be considerably lower than it is in the interior.

(D) Surface irregularities and cracks may extend to some depth so that mechanism (A) may make ineffective a layer of appreciable thickness.

By assuming free diffusion of excitons and destruction at an ideal surface according to (A), we have been unable to account for the experimental results in a satisfactory way. It is possible to get a maximum in the curve of yield *vs* absorption constant, but the maximum is too flat to give as deep a minimum in yield *vs* frequency as is observed.

We have therefore made the more drastic assumption that there is a dead layer of thickness h at the surface

[1] L. Apker and E. Taft, Phys. Rev. **81**, 698 (1951).
[2] L. Apker and E. Taft, Phys. Rev. **79**, 964 (1950).
[3] At lower energies photons eject electrons from F-centers directly, but this process is unimportant here.
[4] U. Fano, Phys. Rev. **58**, 544 (1940).

of the crystal and that there is no production of electrons by excitons in this layer. At greater depths, the production will be supposed to follow Eq. (2). We thereby neglect the effect of diffusion of the excitons which in any case is completely overshadowed by the effect of the dead layer.

III. ELECTRON ESCAPE

As a simple preliminary to the application of age theory to the diffusion and escape of the electrons, we shall calculate the yield using an exponential escape probability[5]

$$P(z)=e^{-\gamma z}. \tag{3}$$

We have then to integrate Eq. (1), replacing the lower limit 0 by h, and using Eqs. (2) and (3). The result is

$$Y=\alpha e^{-(\alpha+\gamma)h}/(\alpha+\gamma). \tag{4}$$

According to Apker and Taft,[1] the maximum yield is about 2.2×10^{-3}, and it occurs at $\alpha=0.6\times10^{6}$ cm^{-1}. These data suffice to fix both γ and h. One finds $1/\gamma=38$A, $h=136$A. The solid curve in Fig. 1 shows the yield Y as function of α, for these values of the parameters.

We now consider more precisely the escape of electrons from the crystal. Let us suppose that electrons are being produced at a depth $z=z_0$ with an initial energy ϵ_0 relative to the bottom of the conduction band.[6] As they diffuse from their origin at z_0, they will gradually lose energy and an electron reaching the surface will have an energy $\epsilon\leqq\epsilon_0$. If ϵ is greater than the electron affinity A, which is the height of the surface barrier above the bottom of the conduction band, then it may surmount the barrier and escape into the vacuum. If $\epsilon<A$, the electron cannot leave the crystal. Actually, an electron with $\epsilon>A$ will not be able to escape unless the energy associated with its motion perpendicular to the barrier exceeds A. In the diffusion problem, this means that a fraction A/e of the electrons impinging on the surface are turned back. However, if the energy loss per collision is small, an electron once reaching the surface will have a large number of opportunities to escape before there is any appreciable change in its energy. Then, if $\epsilon>A$, it will be almost certain to escape. We shall assume that this treatment is sufficiently accurate for our purpose.

The simultaneous diffusion and slowing down of electrons is conveniently treated by the "age theory" of Fermi.[7] Let λ and $\Delta\epsilon$ be the mean free path and mean energy loss per collision. Both may be functions of the energy ϵ. Then the "age," which is actually the square of a length, is defined by

$$\tau=\int_{\epsilon}^{\epsilon_0}\lambda^2 d\epsilon/3\Delta\epsilon. \tag{5}$$

The slowing down density q is defined as the number of electrons per cm^3 which reach energy ϵ or age τ per sec. It satisfies

$$\partial^2 q/\partial z^2=\partial q/\partial\tau.$$

The boundary conditions suitable to our problem are

$$q=0 \text{ at } z=0 \text{ and } z=\infty,\ q=\delta(z-z_0) \text{ at } \tau=0.$$

The last condition specifies a source of one electron per cm^2 per second with energy ϵ_0 (age zero) at depth $z=z_0$. The requirement $q=0$ at $z=0$ implies escape of all electrons reaching the surface. As discussed above, this will be closely true for $\epsilon>A$, which is the only range of interest. It is easily verified that the solution for q is

$$q=\{\exp[-(z-z_0)^2/4\tau]-\exp[-(z+z_0)^2/4\tau]\}/(4\pi\tau)^{\frac{1}{2}}.$$

The flux of electrons of age τ escaping through the surface $z=0$, per cm^2 per sec per unit age is

$$\Gamma(z_0,\tau)=(\partial q/\partial z)_{z=0}=z_0\exp(-z_0^2/4\tau)/(4\pi\tau^3)^{\frac{1}{2}}. \tag{6}$$

To find the escape probability for electrons produced at depth z_0, we have to integrate Γ over the range of

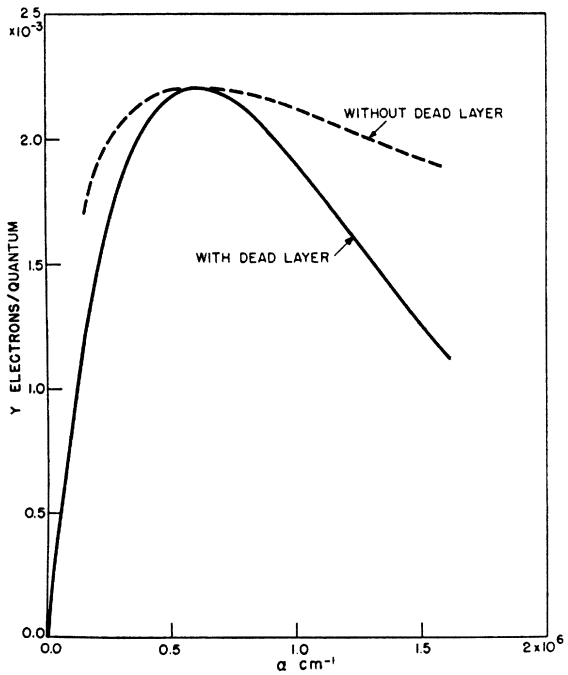

FIG. 1. Dependence of yield on absorption coefficient.

[5] An exponential escape probability has been used by J. A. Burton, Phys. Rev. **72**, 531 (A) (1947) and by N. D. Morgulis, Compt. rend. acad. sci. U.R.S.S. **52**, 675 (1946) for Cs_3Sb surfaces. There it is generally assumed that the electron affinity is zero so that electrons encounter no barrier at the surface. Then the exponential law follows from the assumption of free diffusion together with a uniform bulk absorption of electrons. In the alkali halides, there is no immediate justification for the exponential law.

[6] We have taken the initial energy ϵ_0 the same for all electrons. It would be more realistic to assume a distribution of values corresponding to a spread in energy of the excitons. Such a spread will exist if the excitons are produced with a range of energies or if they are produced with an energy higher than the minimum allowable in the crystal and subsequently lose energy.

[7] E. Fermi, *Nuclear Physics* (Chicago University Press, Chicago, 1950); R. E. Marshak, Revs. Modern Phys. **19**, 185 (1947).

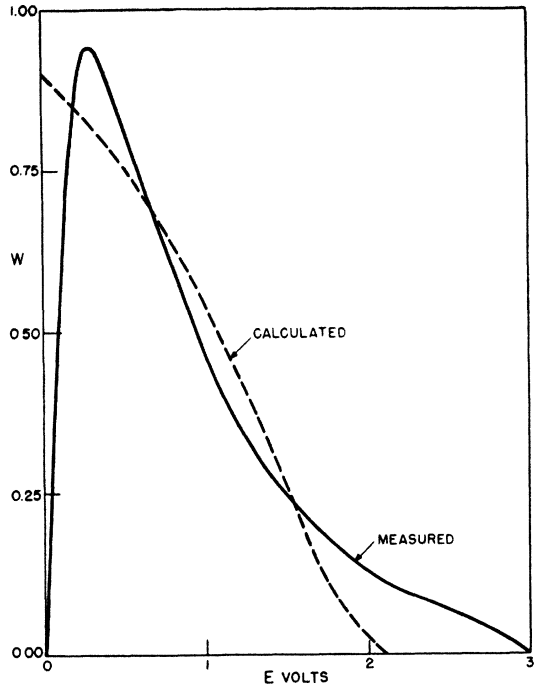

FIG. 2. Energy distribution of photo-electrons from RbI $h\nu=5.56$ volts, $T=300°$K.

ages corresponding to $A<\epsilon<\epsilon_0$. Let the age at which $\epsilon=A$ be τ_a; then the escape probability is

$$P(z_0)=\int_0^{\tau_a}\Gamma d\tau=\int_0^{\tau_a}\frac{z_0\exp(-z_0^2/4\tau)}{(4\pi\tau^3)^{\frac{1}{2}}}d\tau$$
$$=Erfc(z_0/2\tau_a^{\frac{1}{2}}), \quad (7)$$

in which the error integral is defined by

$$Erfc(x)=(2/\pi^{\frac{1}{2}})\int_x^\infty \exp(-x^2)dx.$$

With the escape probability (7), the yield is

$$Y=\int_h^\infty \alpha e^{-\alpha z}Erfc(z/2\tau_a^{\frac{1}{2}})dz$$
$$=e^{-\alpha h}Erfc(h/2\tau_a^{\frac{1}{2}})-\exp(\alpha^2\tau_a)Erfc(\alpha\tau_a^{\frac{1}{2}}+h/2\tau_a^{\frac{1}{2}}). \quad (8)$$

When the parameters h, $\tau_a^{\frac{1}{2}}$ are adjusted to yield a maximum 2.2×10^{-3} at $\alpha=0.6\times10^6$, we find $h=146$A, $\tau_a^{\frac{1}{2}}=50$A. The plot of Eq. (8) is then indistinguishable from Fig. 1 obtained with Eq. (4).

From the data of Apker and Taft, one can estimate that the maximum absorption at 85°K is $\alpha=1.4\times10^6$. According to Fig. 1 the yield is then $Y\simeq1.4\times10^{-3}$. This is to be compared with the yield 1×10^{-3} at the bottom of the valley in the experimental curve. It is apparent that the calculated valley is only two-thirds as deep as that observed.

It was stated earlier that destruction of excitons at an ideal surface in accordance with mechanism (A) could not account for the observations. The broken line in Fig. 1 is obtained with this hypothesis. The parameters used were $\tau_a^{\frac{1}{2}}=47$A and $L=800$A, where L is the diffusion length for the excitons. The curve is so flat that the reduction at $\alpha=1.4\times10^6$ is only a fifth of that required.

The mean free path λ is connected with the age τ by Eq. (5). In order to estimate λ we suppose that the integrand is constant and find

$$\lambda=[3\tau_a\Delta\epsilon/(\epsilon_0-A)]^{\frac{1}{2}}.$$

We have already found $\tau_a^{\frac{1}{2}}=50$A. The difference ϵ_0-A is just the difference in $h\nu$ at the peak and threshold, *viz.*, $5.7-3.0=2.7$ volts. Estimating $\Delta\epsilon=0.05$ volt, we get $\lambda\cong10$A in order of magnitude.

IV. ENERGY DISTRIBUTION OF PHOTO-ELECTRONS

Further evidence in support of the mechanism proposed here and of the existence of a dead layer on the surface comes from a study of energy distribution of the photo-electrons. Preliminary results at room temperature have shown that the exciton-enhanced emission consists predominantly of slow electrons.[8] This fits nicely with the hypothesis of a dead layer, since electrons originating at a depth in the crystal will become degraded in energy on diffusing to the surface. The distribution in age of electrons reaching the surface is

$$W(\tau)=\int_0^\infty S(z)\Gamma(z,\tau)dz$$
$$=(4\pi\tau^3)^{-\frac{1}{2}}\int_h^\infty \alpha e^{-\alpha z}z\exp(-z^2/4\tau)dz$$
$$=\alpha^2\{[1/\alpha(\pi\tau)^{\frac{1}{2}}]\exp(-\alpha h-h^2/4\tau)$$
$$-\exp(\alpha^2\tau)Erfc(\alpha\tau^{\frac{1}{2}}+h/2\tau^{\frac{1}{2}})\},$$

with the help of Eq. (6). The age τ and energy ϵ of the electrons are related by Eq. (5). If we suppose λ and $\Delta\epsilon$ independent of ϵ then

$$\tau/\tau_a=1-E/E_0, \quad (9)$$

where $E=\epsilon-A$ is the kinetic energy of the emitted electron and $E_m=\epsilon_0-A$ is its maximum value.

Figure 2 shows a comparison between the distribution according to Eq. (8) and that measured at $h\nu=5.56$ volts by Apker and Taft.[8] The parameters used in constructing the theoretical curve were $\alpha=0.72\times10^6$, $h=115$A, $\tau_a^{\frac{1}{2}}=50$A, $E_m=2.6$ volts. These were obtained by assuming that the observed yield of 8×10^{-3} electron/quantum at the maximum with respect to $h\nu$ was also the maximum with respect to α. Then h and α are determined if $\tau_a^{\frac{1}{2}}$ is fixed at the value found previously. This procedure is admittedly rough but is probably adequate in view of the preliminary nature of the data. It should be emphasized that the measurements showing self-reversal in the yield, the measurements of optical

[8] L. Apker and E. Taft (to be published).

absorption and the measurements of energy distribution were taken each on a different surface in a different tube. Further, there is good evidence that the parameters, particularly h, vary with the preparation of the surface.[8] One does not seem to be justified, therefore, in attempting a more accurate determination of the constants.

The principal feature of the experimental curve, namely, the steep rise at low energies, is well represented by the theoretical curve. It is not at all surprising that in other respects there are some differences between them. It should be remarked that the comparison of the energy distributions is a more severe test of the theory than comparison of yields, since the latter is a comparison of the integral of the former. Further, to determine the energy distribution, it is necessary to assume an explicit form for the connection between age and energy which is not required for the yield.

The differences between the curves of Fig. 2 can be explained in a reasonable way in terms of the model which we have used. There are two considerations that have been left out of account that will raise the calculated distribution at the high end where it is too low. First, one should expect a gradual transition from the surface dead layer to the active material in the crystal. Thus, some electrons will be able to originate at depths less than h, and these will lose less energy in reaching the surface. Second, one can expect the electrons to be produced with an initial spread in energy of several tenths of a volt.[6] Those that are abnormally energetic at birth will be likely to reach the surface with an excess of energy. Neither of these effects can make any noticeable change in the course of the yield.

At $E=0$ the theoretical curve drops discontinuously to zero. This is to be attributed to our assumption that an electron reaching the surface with $\epsilon>A$ will surely surmount the surface barrier and escape. Actually, when $\epsilon-A$ is small, the chance of escape in a single encounter $(\epsilon-A)/\epsilon$ becomes so small that a large fraction of electrons will lose their extra energy without getting over the barrier. The resulting distribution would decrease continuously to zero in better agreement with observation.

The distribution to be expected when there is no dead layer but destruction of excitons at the surface (mechanism A) has also been calculated. In this case, diffusion of the excitons is taken into account. It turns out then that the distribution in age decreases with increasing age. With the linear connection (9) between age and energy, this means that the energy distribution rises with energy in violent contradiction with experiment. We conclude that a dead layer is essential to the explanation of both the energy distribution and the yield.

It is a pleasure to acknowledge indebtedness to LeRoy Apker and to Harvey Brooks for many stimulating discussions and suggestions and to the latter for the introduction to age theory.

PHYSICAL REVIEW VOLUME 81, NUMBER 5 MARCH 1, 1951

Consequences of Gauge Invariance for Radiative Transitions*

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(Received September 28, 1950)

Consideration is given to any system of particles whose behavior under the influence of an external electromagnetic field can be described by a gauge invariant Schroedinger equation. Detailed restrictions on the form of the hamiltonian which are imposed by the condition of gauge invariance are derived. These provide a simple means to the solution of many problems of the interaction of a system with the electromagnetic field. In particular the following consequences are established: (1) In multipole expansions for single photon processes the electric multipole operators have the usual form but the form of the magnetic multipole operators may depend in a detailed way on the interactions between particles and electromagnetic field. (2) The f-sum rule can be expressed in closed form in terms of the interactions. (3) A generalization of the f-sum rule to all electric multipole orders is given. (4) The cross section for scattering of a low energy photon can be expressed in terms of the electrostatic polarizability quite independently of the interactions. Applications of these methods to problems in nuclear physics are given in an accompanying paper.

I. INTRODUCTION

IT is generally assumed for any molecular, atomic, or nuclear system that, to the approximation in which it can be described by a Schroedinger equation, the electromagnetic interactions of the system must appear in such a way as to leave the equations of motion gauge invariant. The purpose of this note is to show that this assumption has many general consequences for radiative transitions. For example, the well known f-sum rule for the oscillator strengths can be obtained directly from the gauge property as can similar sum rules for the other electric multipole orders.

Since nuclear processes involve charge-bearing quanta

* Supported in part by the U.S. AEC and in part by the Wisconsin Alumni Research Foundation.
† AEC Predoctoral Fellow.