

Intrinsic Photoemission of Alkali Halides

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The photoemission from evaporated films of 12 alkali halides has been measured in the 10- to 21-eV energy region. In addition, some preliminary optical-density values were obtained by measuring the transmission of evaporated layers of these compounds deposited on 450 Å-thick, self-supporting, Al₂O₃ films. The photoemission yield curves show broad structures correlated with the absorption coefficients. In general, the photoemission is a maximum for photons of energies of about 5 eV greater than the forbidden-gap energy E_g , with additional peaks beyond $2E_g$. The correlation of the yield with the absorption coefficient is most pronounced in the alkali fluorides, which have relatively low yields, but is less apparent in the other halides, which have peak values of as much as 0.8 electron/photon. A random-walk model of electron scattering is used to estimate the magnitude of the yields and the dependence on the absorption coefficient, with good qualitative agreement with the experimental results, but other processes cannot be ruled out.

I. INTRODUCTION

RECENT investigations¹⁻⁴ have used the volume photoelectric effect as a means of deducing the electronic properties of solids. The measured quantum yields and electron energy distributions were used to calculate the electron affinity,³ the valence band position and width, and the onset of direct and indirect transitions.¹ Since the photoelectrons are generated in the volume of the solid, the photoelectric yield depends on the transport properties of the substance as well as on its optical properties. Band bending, impurities, and space charges have been shown^{1,5} to affect the yield. The photoelectric effect has been used to estimate the range of "hot" electrons in metals⁶ and semiconductors. The range of photoelectrons in metals is apparently limited by inelastic scattering from conduction electrons. In semiconductors and insulators the electrons undergo nearly elastic scattering from phonons and impurities and inelastic scattering due to the ionization of impurities and the excitation of valence electrons to conduction levels.⁷ The magnitude of the volume photoelectric yield of metals is relatively low (about 0.1 electron/photon),^{8,9} whereas the yield of a pure insulator with a small electron affinity is somewhat greater (about 0.3 electron/photon).^{10,11}

The alkali halides are insulators with large forbidden gaps of about 8 eV and electron affinities of the order of 1 eV.¹² The photoemission of some of the alkali

halides has been measured by Taft and Philipp¹³ and others,^{14,15} and quantum yields in excess of 0.3 have been reported. However, most of the previous work has been limited to investigation of the photoemission in the spectral range of 6 to 11 eV. This paper reports the quantum yields of 12 alkali halides for photon energies of 10 to 21 eV.

II. EXPERIMENTAL

The monochromator was a 1-m scanning monochromator used in the Seya position. The light was dispersed from a 1200 grooves/mm, Bausch & Lomb uncoated aluminum replica grating, which was blazed at 800 Å in first order. Entrance and exit slits were generally set at 90 and 150 μ, respectively, giving a bandwidth of about 1 Å.

The light source was a high-voltage, spark-discharge type, operating at about 10 kc/sec and 12 kV. Helium was used as the source gas for the spectral range 1026 to 584 Å. After passing through a liquid-nitrogen cold trap, the gas flowed through a water-cooled quartz capillary at about 120 mm Hg pressure. A high-intensity helium continuum peaked at 800 Å was produced, in addition to a few dozen superposed impurity lines. A high-speed differential pump behind the entrance slit kept the pressure in the monochromator chamber below 10⁻⁴ Torr during operation of the light source. This type of source was first used by Hopfield,¹⁶ and modifications have been described by Tanaka and others.¹⁷ After an initial warmup period the source was constant to within a few percent, producing a photon flux through the exit slit of about 10⁸ photons/sec. Hydrogen was used in the same lamp for investigations in the 900- to 1300-Å region. A very dense line spectrum was produced at a hydrogen pressure of about 1 mm

¹ G. W. Gobeli and F. G. Allen, *Phys. Rev.* **127**, 141 (1962).

² W. E. Spicer and R. E. Simon, *Phys. Rev. Letters* **9**, 385 (1962).

³ D. Brust, M. Cohen, and J. Phillips, *Phys. Rev. Letters* **9**, 389 (1962).

⁴ E. O. Kane, *Phys. Rev.* **127**, 131 (1962).

⁵ J. J. Scheer, *Philips Res. Rept.* **15**, 584 (1960).

⁶ C. R. Crowell, W. G. Spitzer, L. E. Howarth, and E. E. LaBate, *Phys. Rev.* **127**, 2006 (1962).

⁷ E. Taft, H. Philipp, and L. Apker, *Phys. Rev.* **110**, 876 (1958).

⁸ W. Walker, N. Wainfan, and G. Weissler, *J. Appl. Phys.* **26**, 1366 (1955).

⁹ W. C. Walker, G. L. Weissler, *J. Quant. Spectry. Radiative Transfer* **2**, 613 (1962), and references therein.

¹⁰ W. E. Spicer, *Phys. Rev.* **112**, 114 (1958).

¹¹ E. Taft and L. Apker, *J. Opt. Soc. Am.* **43**, 81 (1953).

¹² J. Eby, K. Teegarden, and D. Dutton, *Phys. Rev.* **116**, 1099 (1959).

¹³ E. A. Taft and H. R. Philipp, *Phys. Chem. Solids* **3**, 1 (1957).

¹⁴ J. Taylor and P. L. Hartman, *Phys. Rev.* **113**, 1421 (1959).

¹⁵ J. N. Lloyd, thesis, Cornell University, 1963 (unpublished). See also the data in P. L. Hartman, *J. Quant. Spectry. Radiative Transfer* **2**, 579 (1962).

¹⁶ J. J. Hopfield, *Phys. Rev.* **35**, 1133 (1930), and **36**, 784 (1930).

¹⁷ R. Huffman, Y. Tanaka, and J. Larrabee, *J. Opt. Soc. Am.* **52**, 851 (1962), and references therein.

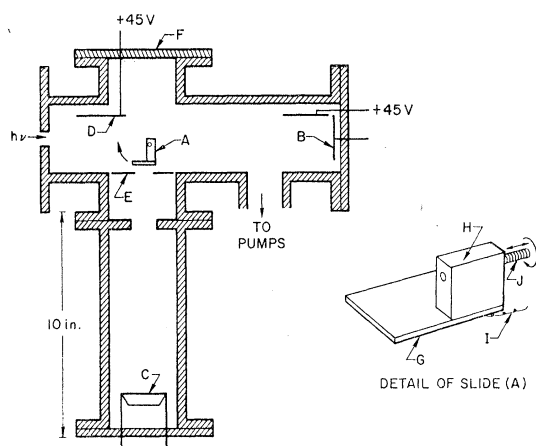


FIG. 1. Diagram of the experimental chamber (semischematic). The slide (A) is shown in the evaporation position; for measurements, it is rotated 90 deg clockwise into the beam. B is the detector; C, the boat; D, the collector; E, the collimator; F, the Lucite plate; G, the glass slide; H, the insulator; I, the lead wire; J, the rotary seal shaft.

Hg; the most intense lines gave about 10^9 photons/sec through the exit slit.

The alkali halides were evaporated *in situ* upon metallized glass slides which could then be rotated into measurement position (Fig. 1). A flexible copper wire made contact with the metallized slide and went to a standard glass-Kovar lead-through. The slides were made by evaporating a semitransparent film of aluminum or nickel upon glass microscope slides. Semitransparent conducting films were used so that the evaporation could be visually monitored by looking through the Lucite top plate, through the slide, and down into the molybdenum boat. The slide was also used as a shutter during an evaporation by moving it forward and back parallel to the axis of rotation. In the initial stage of evaporation one part of the slide covered the $\frac{3}{4}$ -in.-by- $\frac{3}{4}$ -in. collimation hole; once evaporation was proceeding well, the slide was moved to a new position and held there a few moments until a coating of one or two interference layers was built up; the slide was then returned to the original position.

The evaporation was usually done with crushed optical quality crystals, but sometimes reagent grade powder was used. The photoyield of an alkali halide evaporated from powder form was identical, within experimental error, to the yield of the film evaporated from crushed crystals. The pressure during evaporation was somewhat higher than might be desired, being about 5×10^{-5} Torr. After evaporation the pressure fell an order of magnitude very quickly if the 2-in. diffusion pump connected to the experimental chamber was properly cold-trapped. However, with the light source operating, the pressure was about 5×10^{-5} Torr if helium was being used; somewhat lower pressures were obtained during runs at longer wavelengths with hydrogen used as the lamp gas.

The absolute value of the photon flux was determined by use of a calibrated platinum detector. Once the photoyield, Y_{Pt} , of the platinum foil was determined, the absolute yield of the compounds measured could be computed. The absolute yield of platinum was measured in this laboratory in the following manner.¹⁸ An ion chamber was constructed consisting of two parallel plate electrodes extending from the platinum photocathode at one end of the 30-cm chamber to within 2 cm of the exit slits of the monochromator. The current collected by these electrodes is

$$I_g = Y_g e I N_0 [1 - \exp(-n\sigma L)],$$

where Y_g = ionization efficiency of the gas, N_0 = number of photons/sec, and $n\sigma L$ = optical density of the gas. The current from the platinum photocathode is

$$I_{Pt} = Y_{Pt} e I N_0 \exp(-n\sigma L).$$

For the rare gases, argon, krypton, and xenon, it is assumed that the ionization efficiency is unity above the $^2P_{1/2}^0$ limit. Thus the slope of a plot of I_g versus I_{Pt} is equal to $-1/Y_{Pt}$. One might worry that ions formed near the slits might not be collected. It can easily be shown that if the effective distance of non-collection is of length x , then the fractional error in the computed value of Y_{Pt} will be $(x/L) \exp(+n\sigma L)$. Evidently x was very small in this work, for the values of Y_{Pt} calculated for various values of L and $n\sigma L$ were in very good agreement if $L > 15$ cm and $n\sigma L < 5$. Errors might also be caused by reflected or scattered radiation, electron impact ionization, fluctuations in the density of the gas, etc. These effects were investigated¹⁹ and found to be negligible. The yield found for platinum is in reasonable agreement with the thermocouple measurements of Watanabe and Matsunaga²⁰ and the measurements of Walker, Wainfan, and Weissler.⁸ The platinum calibration curve is plotted in Fig. 2. The solid curve is from the present data for the particular piece of platinum used as the detector; the dashed part of the curve below 11.5 eV is taken from the measurements of Watanabe and Matsunaga on a different platinum foil. Since the present experiment indicated that different platinum foils gave different yields (the difference amounting to as much as 25%), it is possible that the yield values in the 9.0- to 11.5-eV range are in error by that much; that is especially probable at lowest energy, since the onset of volume photoemission is sensitive to surface contaminations. The yield of the platinum foil was checked repeatedly over a period of weeks with little change seen.

Some preliminary measurements of the absorption

¹⁸ A similar procedure has been described by J. A. R. Samson, *J. Opt. Soc. Am.* **54**, 6 (1964).

¹⁹ P. H. Metzger and G. R. Cook, Aerospace Corp. Report ATN-63(9218)-2 (unpublished) and *Bull. Am. Phys. Soc.* **8**, 476 (1963); also, G. R. Cook and P. H. Metzger, ATN-63(9218)-4 (unpublished) and *J. Chem. Phys.* **41**, 321 (1964).

²⁰ K. Watanabe (private communication).

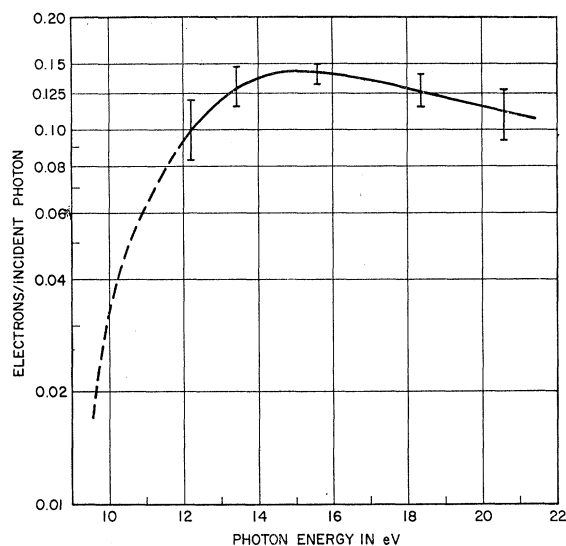


FIG. 2. Photoyield of the platinum detector. The dashed segment is taken from the thermocouple measurements of Matsunaga and Watanabe on another foil. The vertical lines indicate the scatter of a few of the calibration points.

coefficient of these materials were also made. This was done by measuring the transmission of evaporated alkali halide films deposited on self-supporting Al_2O_3 films which were about 450 \AA thick. These films are not difficult to make and are quite durable if proper precautions are observed. The techniques used to make them is a modification of that of Harris.²¹ Strips of commercial aluminum foil, 1 in. by 2 in., were anodized at 32 V in a solution of 19.2 g citric acid and 22.6 g ammonium citrate diluted in a liter of distilled water. The strips were then washed in distilled water and allowed to dry. A circular spot of about $\frac{1}{2}$ -in. diam was painted on the frosty side of a foil with a brush dipped in 8N NaOH. The NaOH dissolves the Al_2O_3 film formed by the anodization and attacks the aluminum beneath. After about five minutes the sodium hydroxide was washed off in distilled water and the foil suspended vertically by means of a pair of tweezers in an 18% solution of reagent HCl, which dissolves the exposed aluminum but does not attack the Al_2O_3 . The films were washed by immersion in distilled water, followed by a neutralizing bath in a 10% solution of ammonium hydroxide and then by repeated washings in several beakers of distilled water. The films will stand a surprising amount of agitation during the washing steps. A small hole previously punched in one corner of the aluminum strip allowed it to be hung up to dry. The rest of the aluminum foil apparently acted as a sufficiently rigid support for the thin Al_2O_3 films, but there was enough "give" to keep the films from cracking as they dried. Over 90% of these films were mounted unbroken in the vacuum chamber, but if the foil was

²¹ L. Harris, *J. Opt. Soc. Am.* **45**, 27 (1955).

constrained in some holder while the film was being formed or drying, the percentage of unbroken films was low. After having dried, the foils were attached (by the aluminum part) to a holder with ordinary vacuum grease. The films are taut and shiny and appear to be fairly smooth substrates for evaporation. The transmission of these Al_2O_3 films is not very high—about 1% at 900 \AA and somewhat less at shorter wavelengths—so an "open" photomultiplier with a Be-Cu photocathode was used as a detector for the transmission measurements.

III. RESULTS

The solid curves with open circles in Figs. 3a through 3l are photoelectric quantum yields. The dotted curves are optical density measurements taken from Milgram and Givens²² for LiF, from Hartman²³ for NaCl and KCl, and from Eby, Teegarden, and Dutton¹² for the rest. The dashed curves are the preliminary optical density measurements from the present experiment. These latter have been multiplied by a factor to form a smooth continuation of the measurements by others at longer wavelength. All measurements were taken at room temperature. The data points shown on the yield curves are averages of a number of runs on different films. In general, the yields agreed very well from run to run on a relative scale, although the absolute values sometimes differed by as much as 15%. An exception was NaF, which gave low and unstable yields. Since this compound seemed to attack the molybdenum boat (this was not true of the other alkali halides), new evaporations were done from an outgassed Al_2O_3 crucible. The yields from these films were higher, as shown, and constant from film to film. All of the alkali halides have yields much higher than the low (0.1) yield of the metallic substrate.

The optical density curves were computed from only one evaporated film of each compound, so the results are probably not too precise, although the agreement with Hartman's values and those computed by Philipp and Ehrenreich²⁴ from reflectivity measurements on single crystals is very encouraging. The reflectivity measurements were taken from (100) faces which had been exposed to air, whereas the vacuum evaporated films apparently form crystallites with the (110) or (221) planes exposed.²⁵ It should be noted that no reflectivity corrections were made in these preliminary measurements. Since the films transmitted only about 10 to 20% of the incident light, such a correction would be fairly small but would tend to depress the absorption peaks somewhat. The transmission measurements were taken on films of evaporated Harshaw single crystals, with the exception of the KF film, which was evaporated from reagent quality powder.

²² A. Milgram and M. P. Givens, *Phys. Rev.* **125**, 1506 (1962).

²³ P. L. Hartman, Ref. 15.

²⁴ H. R. Philipp and H. Ehrenreich, *Phys. Rev.* **131**, 2016 (1963).

²⁵ L. G. Schultz, *J. Chem. Phys.* **17**, 1152 (1949).

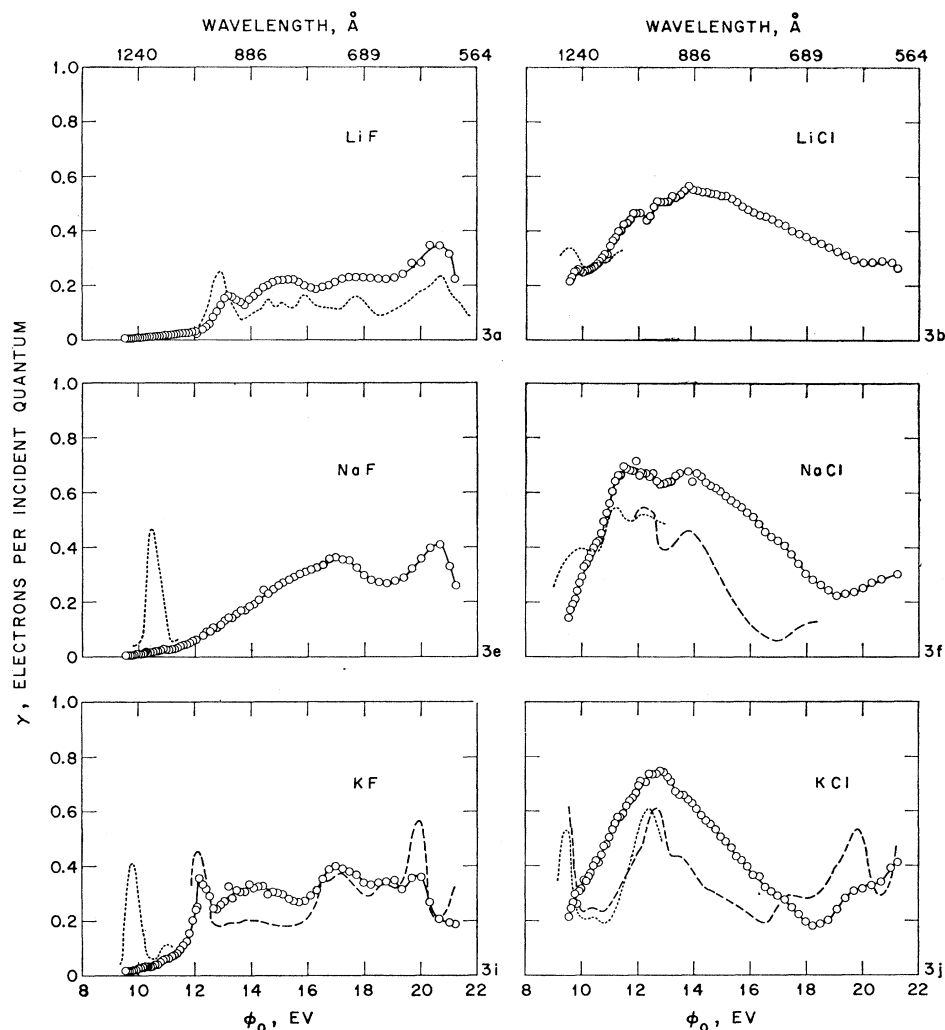


FIG. 3.

One of the striking things about the photoemission from these compounds is the high yield—as much as 80% at some energies. These may be the highest yields ever reported for any substance under ultraviolet irradiation.²⁶ A second remarkable characteristic of the yield curves is a pronounced structure, which seems correlated with the absorption coefficient. It is interesting to note that little photoemission occurs upon irradiation in the exciton band in KF and NaF as would be expected, but photoemission is found in the exciton region in LiF as have been reported before.^{14,15} This peak in the photoemission would be even larger and displaced slightly toward longer wavelengths if corrections were made for the high reflectivity⁹ of LiF near the exciton peak.

IV. DISCUSSION

It has often been stated that the maximum possible photoelectric quantum yield is 0.5. We shall attempt

²⁶ The yield of MgO, another ionic crystal, was found to be

to indicate here that this is not the case, that there are a number of possible mechanisms which could give yields well over 0.5. One process is that in which two electrons are sometimes emitted for one photon: some of the energetic photoelectrons ionize other electrons from surface or impurity states, and two low-energy photoelectrons are produced. Another mechanism involves scattering of the electrons. If the electrons can random walk in the lattice for a long time before being trapped or degraded in energy, the probability is high that they will eventually diffuse to the surface and escape. We shall show that this latter process may occur in the alkali halides by using a random walk analysis similar to that used by Hebb²⁷ to describe the diffusion of *F*-center electrons released by excitons, and by Dekker²⁸ to describe secondary electron emission.

nearly 0.5 and rising at 11 eV, where the measurements stopped, by J. R. Stevenson and E. B. Hensley, *J. Appl. Phys.* **32**, 166 (1961).

²⁷ M. H. Hebb, *Phys. Rev.* **81**, 702 (1951).

²⁸ A. J. Dekker, *Solid State Phys.* **6**, 251 (1958).

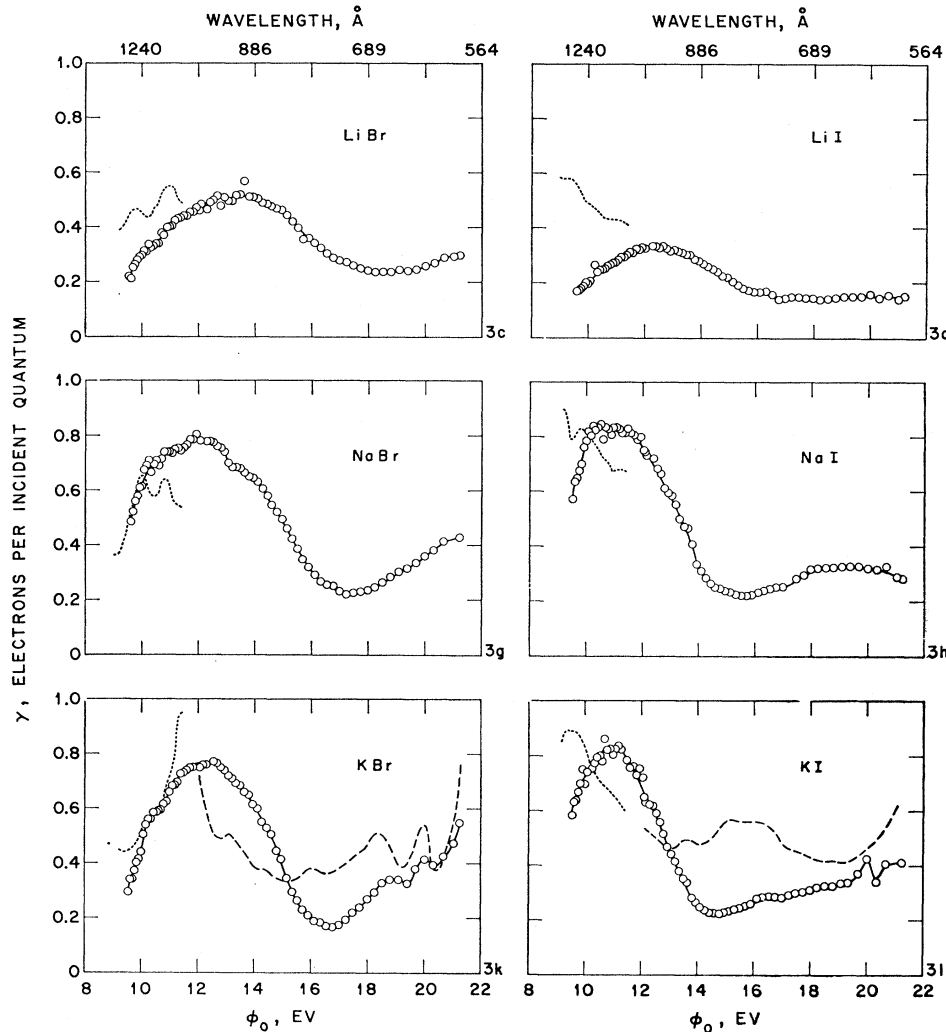


FIG. 3. Photoyields of the alkali halides. Some optical density values are also shown. The dashed curves are our optical density measurements; the others are due to Milgram and Givens (Ref. 22) for LiF, to Hartman (Ref. 23) for NaCl and KCl, and to Eby, Teegarden and Dutton (Ref. 12) for the rest. ϕ_0 is the photon energy in electron volts.

The number of photoelectrons emitted for light of a certain frequency may be written

$$N_e = \int_{x=0}^{\infty} \int_{E'=0}^{h\nu} n(E',x)P(E',x)dE'dx,$$

where $n(E',x)dx$ is the number of photoelectrons created in the solid between x and $x+dx$ with energy E' above the vacuum level, and $P(E',x)$ is the escape probability of these electrons. The upper limit of integration may be set equal to ∞ since the films are much thicker than the absorption distance of the light and the "escape distance" of the photoelectrons. Evidently $\int_0^{\infty} n(E',x)dE'$ must be proportional to $-dI = I_0\alpha \exp(-\alpha x)dx$, where α is the absorption coefficient of the compound and I_0 is the number of incident photons/unit time. The valence bands are narrow in the alkali halides, so $n(E',x)$ will be nonzero for only a narrow range of E' . If $P(E',x)$ varies slowly

with E' in this region, one can write.

$$Y = \frac{Ne}{I_0} \approx \rho \int_0^{\infty} \alpha \exp(-\alpha x)P(\bar{E}',x)dx,$$

where ρ is the fraction of absorbed quanta which produce electrons of average energy \bar{E}' . To obtain an expression for $P(\bar{E}',x)$, consider a random walker starting at x and taking n steps/unit time. If the lifetime of the walker is t_0 , the probability that the walker will reach $x=0$ before t_0 is approximately²⁹

$$P(t_0,x) \approx (2/\pi)^{1/2} \int_{x/\sigma(n t_0)^{1/2}}^{\infty} \exp(-u^2/2)du,$$

where σ is the root-mean-square step length in the direction normal to the crystal surface. In this random-walk model of photoelectron diffusion, t_0 will, in general, be a function of \bar{E}' . Since the electron affinities are

²⁹ P. Erdős and M. Kac, Bull. Am. Math. Soc. 52, 292 (1946).

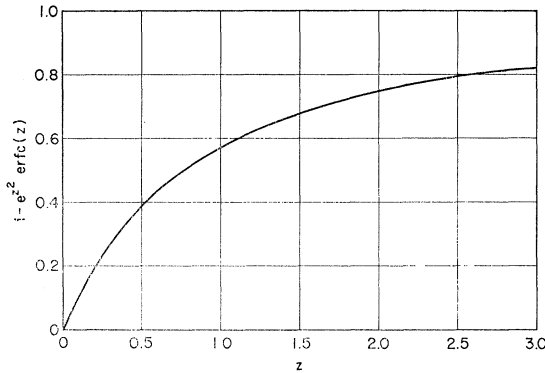


FIG. 4. Plot of the function $1 - e^{-z^2} \operatorname{erfc}(z)$. This function is proportional to z for small z , and approaches $1 - (1/\pi^{1/2}z)$ for large z .

small in the alkali halides, most of the electrons which reach $x=0$ will escape; thus

$$\begin{aligned} Y &\approx \rho \int_0^\infty \alpha \exp(-\alpha x) P(t_0, x) dx \\ &= \rho (1 - \exp[-z^2] \operatorname{erfc} z), \end{aligned}$$

where $z = \alpha \sigma (\frac{1}{2} n t_0)^{1/2}$. It can easily be shown that

$$\begin{aligned} 1 - \exp(-z^2) \operatorname{erfc} z &\approx (2/\pi^{1/2})z & z < 0.2, \\ &\approx 1 - (1/\pi^{1/2}z) & z > 2.5. \end{aligned}$$

A plot of Y/ρ is shown in Fig. 4. Numerous authors have used escape probabilities of the form $\exp(-x/L)$, where L is the "escape distance." Using $2/\pi^{1/2} \exp(-x/L)$ as the escape probability in computing the yield, one obtains

$$Y \approx \rho \left(\frac{2}{\pi^{1/2}} \right) \frac{z}{(1+z)},$$

where $z = \alpha L$, which is a very good approximation to the previous expression for $z \leq 3$.

The root-mean-square scattering length is easily computed. If the electron scattering is isotropic, the distribution of step lengths in three dimensions is $\exp(-r/\lambda)/4\pi r^2$, where λ is the mean free path in three dimensions. The projection of this on the x axis is

$$T(x) = \frac{1}{2\lambda} \int_1^\infty \left[\exp\left(-\left|\frac{x}{\lambda}\right|y\right) / y \right] dy.$$

Hence

$$\sigma^2 = \int_{-\infty}^\infty x^2 dx \frac{1}{2\lambda} \int_1^\infty \left[\exp\left(-\left|\frac{x}{\lambda}\right|y\right) / y \right] dy = \frac{2}{3} \lambda^2.$$

This gives $z = \alpha \lambda (N/3)^{1/2}$, where N is the total number of steps. The quantity N may be limited by two processes: the electron may be trapped or may ionize an impurity state after traveling a distance d (on the average), or it may lose its energy in collisions with phonons. For the

first process, $N = d/\lambda$; for the second, $N = \bar{E}'/\hbar\omega$, where $\hbar\omega$ is the average phonon energy. For this latter case, $z = \alpha \lambda (\bar{E}'/3\hbar\omega)^{1/2}$.

It can be seen from Fig. 4 that the yield of 0.75, such as was measured, corresponds to a value of z of about 2.0. It will be shown that this implies a physically reasonable value for the mean free path. For the alkali halides,²⁴ $\alpha \approx 10^6 \text{ cm}^{-1} = 10^{-2} \text{ \AA}^{-1}$ and $\hbar\omega \approx 1/30 \text{ eV}$; for $\bar{E}' \approx 3 \text{ eV}$, the value $\lambda = z/\alpha (N/3)^{1/2} \approx 2.0/10^{-2} (30)^{1/2} \approx 35 \text{ \AA}$ is obtained. This value is in good agreement with the results of a calculation by Seitz,³⁰ who considered the effect of both optical and acoustic phonons on energetic electrons in NaCl. His estimate of $5 \times 10^{-14} \text{ sec}$ for the collision time implies $\lambda = 50 \text{ \AA}$ for 3-eV electrons, if $m^*/m = 1$. His work also indicates that the scattering is nearly isotropic for electrons of these energies and that the scattering cross sections do not vary much as a function of electron energy. In addition, Shchemelev *et al.*,³¹ looking at the yield of secondary electrons produced by x-ray photoelectrons in alkali halides, estimate an "escape depth" [presumably of the order of $\lambda(N/3)^{1/2}$] of about 600 \AA .

The fact that the compounds with low photoyields (e.g., LiF, KF) show a more pronounced correlation between the yield and the absorption coefficient than the high-yield compounds is easily understood in terms of the model. The derived expression for the yield shows $Y \sim z \sim \alpha$ for small z , whereas $Y \sim [1 - (1/\pi^{1/2}z)]$ for large z . Physically, this means that for compounds in which the electrons can move fairly easily, it does not make too much difference what the average distance ($1/\alpha$) is at which the photoelectrons are generated, but for low-yield compounds, only the electrons produced very near the surface ($dN \sim dI \sim \alpha$) are able to escape.

It should be emphasized that although the data seem to be consistent with the multiscattering diffusion process, that mechanism is by no means proven here. It can, however, be shown that the 2-for-1 impurity ionization process mentioned previously is rather unlikely. Consider a model in which a primary photoelectron can ionize an impurity (with an absorption coefficient for this $n\sigma = 1/L_1$), producing two low-energy electrons which may be absorbed by the lattice (absorption coefficient $1/L_2$). The external emission is composed of those primary and secondary photoelectrons which pass through the surface before they can be absorbed. The expression for the yield which can be derived from this model is proportional to α for low yields and can reach values of nearly unity. However, for these high yields to occur, it is necessary that $L_1 < 50 \text{ \AA}$ and $L_2 > 200 \text{ \AA}$. The first requirement means that the concentration of ionizable impurities must be greater than a few percent, and the second that this model also requires that the electrons undergo numerous

³⁰ F. Seitz, *Phys. Rev.* **76**, 1376 (1949).

³¹ V. Shchemelev, M. Rumsh, and E. Denisov, *Fiz. Tverd. Tela* **5**, 1132 (1963) [English transl.: *Soviet Phys.-Solid State* **5**, 827 (1963)].

lattice scatterings, if Seitz's estimate of 50 Å for the mean free path is correct.

This mechanism would also predict peaks or shoulders due to the ionization onset in the photoyield that are uncorrelated with the absorption coefficient; this does not seem to be the case (cf. NaCl, KCl). In addition this model would predict that the majority of photoelectrons from NaCl and KCl would have energies of less than an electron volt for $h\nu=12$ eV, in disagreement with the observations of Taylor and Hartman¹⁴ and Newburgh.³² However, these investigators used surfaces which had been exposed to air and which were possibly different from those used here.

The photoyield curves for the higher energy photons have some very interesting features, which can be discussed in terms of the electron diffusion escape model; but most of the tentative conclusions presented here are independent of the actual escape process. In the potassium halides, at a few electron volts past the main peak, the photoyield begins to fall more steeply than would be predicted due to the fall of the absorption coefficient in this region. The most probable reason for this is that some of the electrons are energetic enough to produce excitons or to ionize valence electrons. This process should begin to occur at an energy equal to the gap energy plus the energy of the edge of the exciton peak. At 300°K this energy should be about 14.0 and 11.5 eV for KBr and KI, respectively.^{12,33} This compares well with the energies of 13.8 and 11.4 eV, at which the photoemission seems to start falling steeply.

The rise in photoyield at higher photon energies is probably due to the fact that in this energy region the primary photoelectrons can ionize a valence electron and still have enough energy left to escape. Both primary and secondary photoelectrons can escape for photons of energy greater than twice the photoemission threshold. (Because of momentum conservation requirements the ionization thresholds are shifted to somewhat higher energy,³⁴ but only slightly so in the alkali halides, which have narrow valence bands.) The yields are seen to rise at twice the photoemission threshold energy. The occurrence of valence-band ionization by fast photoelectrons has also been suggested by Taylor and Hartman¹⁴ in their analysis of

photoelectron energy measurements on NaCl and KCl.

It is probable that a number of effects and mechanisms contribute to some extent to the observed yields. For example, surface charges or band-bending could greatly modify a diffusion-type process. A band-bending which would increase the photoyield would inhibit the drift of electrons into the crystals, which would reduce the photoconductivity near the surface, in agreement with the null results of Taylor and Hartman.¹⁴ Other factors which could influence the yield are the simultaneous excitation of two electrons by one photon,^{35,36} the excitation of plasma oscillations,^{24,37} and the excitation of lower lying valence bands.²⁴

Finally, it should be noted that although this work agrees in many respects with the work of others, there are definitely areas of disagreement. The work of Lloyd¹⁵ on LiF in the 10- to 21-eV range shows a yield about 40% higher than the present value. The work of Taft and Philipp¹³ on the alkali iodides and the potassium halides in the 10- to 11-eV range shows yields from one-half to one-third of those measured in this experiment. The relative yields (e.g., yield of LiI/yield of KI) measured by the latter investigators are in good agreement with this work. It is not known whether the discrepancy in the magnitude of the yields is due to calibration error or to sample preparation. Work is presently being conducted on the effect on the yields of vacuum conditions, temperature, and film anneal. In addition, the photoemission and absorption coefficient measurements are being extended to the rubidium and cesium halides.³⁸

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³⁵ D. L. Dexter, *Phys. Rev.* **126**, 1962 (1962).

³⁶ T. Miyakawa, *J. Phys. Soc. Japan* **17**, 1898 (1962).

³⁷ P. E. Best, *Proc. Phys. Soc. (London)* **79**, 133 (1962).

³⁸ Further work on the 20 alkali halides (Li, Na, K, Rb, and Cs combinations of F, Cl, Br, and I) indicates that the Rb and Cs series show similar characteristics to those reported here. Repeated calibrations of the flux distribution of the Hopfield helium continuum by rare-gas ionization, indicate good agreement in the 12 to 15 eV region, but the yields reported here are apparently low by 20% at 18 eV and 40% near 21 eV.

³² R. G. Newburgh, *Phys. Rev.* **132**, 1570 (1963).

³³ J. C. Phillips, *Phys. Rev. Letters* **12**, 142 (1964).

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