Photoelectric Emission from *F*-Centers in KI

L. APKER AND E. TAFT
General Electric Research Laboratory, Schenectady, New York
(Received May 16, 1950)

F-centers were produced in thin evaporated layers of KI by ultraviolet irradiation or by electron bombardment. Photoelectric emission became measurable for $h\nu = 2.5$ ev and increased to a plateau value near 10^{-4} electron/quantum at 4 ev. Yields rose further to a sharply peaked value about 20 times higher at 5.66 ev. This point is practically coincident with the first optical absorption maximum for pure KI as measured by Fesefeldt. The peak shifted with temperature in the same way as the optical absorption. The yield was roughly proportional to the absorption constant. Below 5 ev, the emission was attributed to direct ionization of *F*-centers. The enhanced yields at the peak were tentatively ascribed to ionization of centers by excitons produced in the optical absorption.

I. INTRODUCTION

IT has been known for many years that alkali halides containing *F*-centers show an external photoelectric effect.[1] The process, however, has not been very well understood. Several theories have been proposed.[2]

This paper presents new data taken on KI over an extended frequency range. The results suggest that two kinds of emission are possible. First, for photon energies $h\nu$ less than about 5 ev, *F*-centers are ionized directly; some of the electrons escape through the crystal surface. Second, a new phenomenon overshadows this direct ionization near $h\nu = 5.63$ ev, the peak in the first absorption band[3] of pure KI. Theoretical interpretation of this band indicates that the incident photons create excitons.[4] In the experiments described here, these apparently ionize *F*-centers in a secondary process; again, some electrons escape from the crystal.

Topics will be discussed as follows: Section II, pertinent experimental procedures not described elsewhere; Section III, production of *F*-centers in the samples; Section IV, frequency variation of the photoelectric yields, and the onset of enhanced emission.

II. EXPERIMENTAL DETAILS

Figure 1 shows the type of photo-tube used, an improved version of those previously described.[5] It was used in the same way as its predecessors, except that data could be taken as a function of emitter temperature. Reproducibility was established for 10 surfaces in four tubes.

The KI was evaporated from platinum boats onto bucket-shaped Ni or Ta emitters held near 300°K. Film thicknesses on the buckets were computed from interference patterns on the tube walls and ranged from less than 10^{-4} to 10^{-3} cm. Emitter temperatures were estimated from thermocouple measurements on dummy tubes and from the decrease in permeability of Ni buckets at the Curie point.

Precautions were taken to insure that the photoelectric currents were not limited by the electrical conductivity of the samples. The emission saturated at an applied field below 1 v/cm. From this point up to 1000 v/cm, it rose at a rate several times larger than that corresponding to a normal Schottky effect for a metal. Currents were proportional to the intensity of the incident radiation over a range of at least one decade. Except for negligible changes due to the decline in *F*-center concentration, they were constant in time when the radiation was applied to the surface. (Variations occurring within 2 seconds after the radiation struck the surface would have escaped notice, however, since this was the limit imposed by the response time of the current detector.) The results were not dependent on sample thickness. Metal films deposited on the KI showed no evidence of spurious current limitation. Thus, although the KI surfaces showed evidence of patch structures, the emission had the characteristics expected for a normal external photoelectric effect.

III. PRODUCTION OF *F*-CENTERS IN THE EMITTERS

Before irradiation in the general region of the first absorption peak at $h\nu = 5.63$ ev, samples showed no photoelectric emission. Yields varying from 3×10^{-9} electron/quantum at $h\nu = 2$ ev to 3×10^{-6} at 6 ev could have been detected.

At room temperature, 2×10^{11} quanta sec.$^{-1}$ cm^{-2} at $h\nu = 5.66$ ev were then allowed to strike the KI. Photoelectric emission became measurable in a few seconds. It rose as shown in Fig. 2. The first part of this characteristic has very roughly the form expected for a first-order reaction. In drastically oversimplified terms, it may be useful to describe it at this point as follows. A fixed number of vacant iodine ion sites capture electrons

[1] R. Fleischmann, Zeits. f. Physik **84**, 717 (1933).
[2] G. Maurer, Zeits. f. Physik **118**, 104 (1941); E. Asmus, Ann. d. Physik **26**, 723 (1936); T. Muto, J. Phys. Soc. Japan **2**, 193 (1947).
[3] H. Fesefeldt, Zeits. f. Physik **64**, 623 (1930).
[4] For discussion and references, see F. Seitz, Rev. Mod. Phys. **18**, 384 (1946) and NDRC reports on which this paper was based; *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1940). See also reference 6.
[5] For many features of this design, we are greatly indebted to Miss Jean Dickey, who has used them in work on BaO. For a review, see J. A. Becker, Elec. Eng. **68**, 937 (1950). For other details, see Apker, Taft, and Dickey, Phys. Rev. **76**, 270 (1949); **75**, 1181 (1949); **74**, 1462 (1948); **73**, 46 (1948); Ind. Eng. Chem. **40**, 846 (1948).

from a constant density of excitons produced by the incident radiation. (The delayed approach to saturation may be due to other important and more complex processes discussed by Seitz in the references of footnote 4.) F-centers produced in this way give rise to an external photo-current proportional to their density.

When the irradiation was stopped (except for the negligible periods required to measure yields), the photo-current decreased with time. At 300°K, it decayed to 25 percent of its original value in about 60 hr. At 400°K, the same effect took place in 8 min., as shown in Fig. 2. The decay has the form expected for a second-order process. Assuming that the temperature dependence is fixed by the usual exponential Boltzmann factor, one concludes that an activation energy of the order of 0.7 ev is involved. This is in reasonable agreement with the thermal ionization energy,[6] 0.8 ev, of F-centers in KI. We take this as an indication that we are dealing with the well-known kind of F-center rather than with an unusual variety conceivably existing, for example, at surfaces. This point will be mentioned again.

The emitter in some cases was bombarded with 3 ma of electron current at 200 v for 2 sec. The electrons struck the total area 0.64 cm^2 of the end of the bucket. This type of treatment is believed to produce an F-center density of the order of magnitude 10^{19} cm^{-3} in evaporated layers of KCl.[7] Now the photoelectric yield measured directly afterward on the KI emitters was only about twice as high as when the centers were formed by ultraviolet irradiation. If most of the incident 5.66-ev photons in the latter case were absorbed[6] in a distance 2×10^{-6} cm, then 6×10^{18} quanta/cm^3 were absorbed per minute of irradiation. Let us say, for the moment, that each exciton produced one F-center during the initial stages of the process. Then the data in Fig. 2 indicate a final F-center density of the order 10^{19} cm^{-3} in agreement with the number mentioned above for KCl.

We wish to emphasize an alternative possibility at this point. It is conceivable that the 10^{13} quanta cm^{-2} min.$^{-1}$ incident on the surface during irradiation could go entirely into producing roughly 3×10^{13} centers localized at the KI surface. This is still only about three percent of the number of surface atoms. However, it is difficult to see how the activation energy mentioned above could be so close to that for the usual F-center if this were the case.

IV. SPECTRAL DISTRIBUTION OF THE PHOTOELECTRIC YIELD

Figure 3 shows the spectral distribution of the photoelectric yield for a concentration of F-centers near the limiting value. We attribute the emission below $h\nu=5$ ev to direct ionization of the centers. Some of the excited

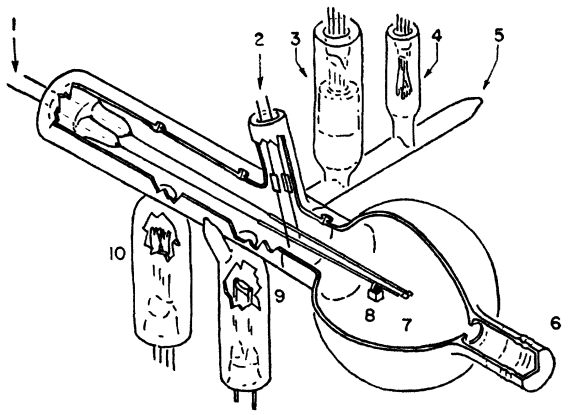

FIG. 1. Cutaway sketch of photo-tube. 1. Lead-in wires to central conductor of hairpin assembly; these two leads are connected by the bucket support 7; inside the collecting sphere they are sheathed by metal tubing supported on insulators. 2. Lead-in wires with spring contacts actuated by armatures; these wires supply current to the sheaths and through them to a small heater filament inside the bucket support 7. 3. Ionization gauge. 4. Getter. 5. Seal-off tip. 6. Quartz window. 8. Typical bucket-shaped emitter; there were eight to ten in each tube. 9. KI evaporator. 10. Evaporator for Ag or Pb [see E. A. Taft and J. E. Dickey, Phys. Rev. **78**, 625 (1950)].

electrons escape through the crystal surface. One notes that the yield rises more slowly near the threshold than in the case of a metal, for example. (This must be interpreted with care, however, because surface patch structures may be pronounced for materials of such low conductivity.)[8] Near $h\nu=4$ ev, the yield reaches a plateau (of $\sim10^{-4}$ electron/quantum) presumably set by the maximum efficiency of ionization and escape from the surface.

It is interesting, therefore, to estimate an order of magnitude for the probability that an F-center will absorb a photon of energy near 5 ev. We assume an oscillator strength $f=0.1$ for a transition to a continuum of effective width $h\Delta\nu=3$ ev, keeping in mind that most of the oscillator strength for an F-center is concentrated near $h\nu=2$ ev in the F absorption band.[4] The cross section for absorption[9] is then $\sigma=(\pi h/mc)(e^2/h\Delta\nu)f=3\times10^{-18}$ cm^2. For an F-center concentration of 2×10^{13} per cm^2 of surface area in the thin KI film, the absorption amounts to 6×10^{-5}. If we assume that half of the electrons escape, the photoelectric yield becomes 3×10^{-5}. This is to be compared with the measured value of 10^{-4} above. The escape probability taken here is very high, but the final result is still too low. The agreement is probably as good, however, as can be expected in such a rough estimate.

As $h\nu$ increases above 5 ev, the optical absorption

[6] R. W. Pohl, Proc. Phys. Soc. **49** (extra part) 3 (1937); J. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, London, 1935).

[7] F. Seitz, reference 4 and work cited there.

[8] C. Herring and M. H. Nichols, Rev. Mod. Phys. **21**, 185 (1949); G. Wannier, Phys. Rev. **76**, 438 (1949); H. M. James, Science **110**, 254 (1949). It must be remembered that the KI emitters under consideration here are not in true equilibrium. The centers are only metastable. Internal currents may be carried by both ions and electrons.

[9] H. Bethe, *Handbuch der Physik*, Vol. 24/1, p. 429; H. Fröhlich and R. A. Sack, Proc. Phys. Soc. London **59**, 30 (1946).

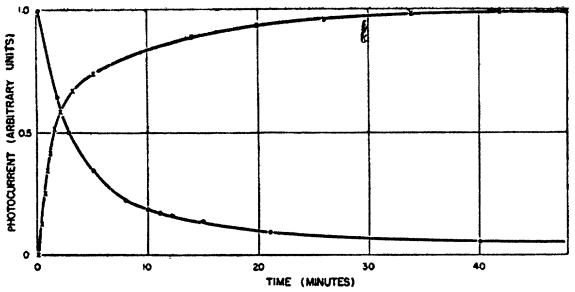

FIG. 2. Increase of photo-current at $h\nu = 5.66$ ev as F-centers form in emitter (crosses). Decrease of current at approximately 400°K as centers are destroyed thermally (circles).

increases to its maximum value at 5.63 ev. This is shown by Fesefeldt's data[3] plotted on a logarithmic scale in Fig. 3. The photoelectric yield rises to a pronounced peak at 5.66 ev. The small difference is probably within the experimental error. The yield is roughly proportional to Fesefeldt's optical absorption coefficient and reaches a value 20 times higher than that on the plateau. (This factor varied from 8 to 50 for various samples.) At a temperature of 400°K, the photoelectric peak was broadened and displaced to $h\nu = 5.55$ ev, in

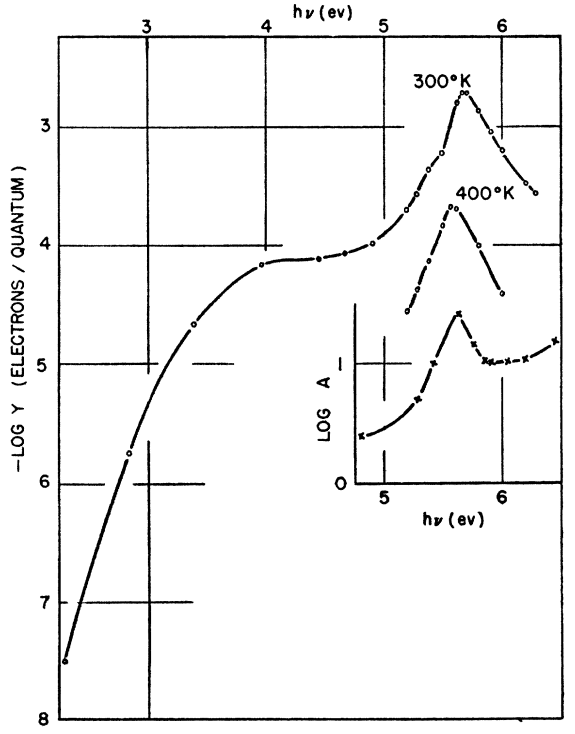

FIG. 3. Spectral distribution of the photoelectric yield Y in electrons/quantum for KI with F-centers. The small inflection just to the left of the peak on the curve for 300°K is reproducible and apparently real. Fesefeldt's values of the optical absorption constant A (in arbitrary units) for KI at 293°K are given on a logarithmic scale below the photoelectric data.

agreement again with Fesefeldt's data. The lower yield at the higher temperature was due to the partial destruction of the F-centers before the measurements were made.

Suppose we tentatively assume that the electrons escaping from the crystal originate in a layer of thickness 10^{-6} cm or less next to the surface. This is less than the photon mean free path at 5.63 ev, where the absorption has its maximum. In accordance with previous interpretations of this absorption, we attribute it entirely to exciton production.[4] Then the number of excitons produced in the thin layer is proportional to the absorption constant at the value of $h\nu$ under consideration. Thus the results described in the paragraph above are to be expected if the photoelectric yield is proportional to the product of the densities of F-centers and excitons in the layer.

When the density of F-centers was lowered, the photoelectric yield decreased in approximately the same ratio at all values of $h\nu$. Thus, the yield due to direct ionization was proportional to the enhanced emission. If we assume that the first type of emission was proportional to the F-center density, we conclude that the second was also. This agrees with the hypothesis above and with the linearity shown by the initial portion of the activation curve in Fig. 2. Since the photoelectric yield in the peak is only 2×10^{-3} electron/quantum, we must conclude that only a small fraction of the exciton is effective in producing external emission.

V. CONCLUDING REMARKS

The main point suggested here is that excitons can increase the efficiency of photoelectric emission from F-centers by more than an order of magnitude. If accepted, it constitutes evidence for exciton mobility. The conclusion rests almost entirely on the surprisingly close similarities between Fesefeldt's optical absorption data and the photoelectric measurements given here. It indicates the possibility of photo-conductivity with an analogous origin. The simple models used in this paper seem capable of describing the gross features of the effect. However, they are presented for acceptance with caution, since the phenomena are doubtless more complex in their details than such models imply. Measurements of photo-electron energy distributions, to be submitted later, are capable of giving greater insight into the processes involved.

We wish to thank Katherine B. Blodgett for the interference step gauge used in making thickness measurements on the thin films. Jean Dickey has given us the benefit of her assistance on frequent occasions. We are grateful to Malcolm Hebb, Harvey Brooks, and Frederick Seitz for their generous interest in this work and for many valuable conversations.