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Exciton-Enhanced Photoelectric Emission from *F*-Centers in RbI near 85°K

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The photoelectric emission from *F*-centers in RbI was measured at 300°K. It was compared with the optical absorption of pure RbI as determined by Fesefeldt's method at the same temperature. The results were analogous to those previously reported for KI, and indicated that exciton-enhanced photoelectric emission reached a peak at $h\nu \sim 5.6$ ev, where the optical absorption had its first maximum. When the films were cooled to 85°K, the exciton-induced emission showed a *double* maximum separated by a sharp minimum at $h\nu = 5.72$ ev. This minimum coincided with the shifted position of the first optical absorption peak at the lower temperature. The spectral distribution of the yield had somewhat the appearance of a self-reversed spectral line. An attractive explanation is that the photoelectric emission at first increases with the optical absorption, reaches a maximum for an absorption constant near 10^6 cm^{-1}, and then decreases as the absorption constant becomes still larger. The decrease is attributed to a sparsity of *F*-centers near the surface, and to a growing destruction of excitons at the surface as the layer in which they are formed becomes thinner. Yields near the photoelectric threshold were compared qualitatively with Herring's theory of photoemission from impurities in a polar crystal. An upper limit of 1.9 ev was placed on the electron affinity of these RbI films.

I. INTRODUCTION

A PREVIOUS report[1] has discussed the photoelectric emission from *F*-centers in KI at 300° and 400°K. For $h\nu < 5$ ev, the emission appeared to be due primarily to direct photon ionization of *F*-centers. For $h\nu > 5$ ev, however, excitons formed in the fundamental absorption band of the pure KI apparently ionized the centers in a secondary process. As a result, the photoelectric yield was enhanced by more than an order of magnitude. It showed an extremely sharp maximum at $h\nu = 5.66$ ev, a point essentially coincident with the first fundamental optical absorption peak as determined by Fesefeldt.[2]

This paper reports subsequent experiments on RbI. The measurements were carried out both at 300°K (where the results were like those for KI) and at 85°K. At the lower temperature, a new phenomenon became evident. The spectral distribution of the yield showed two maxima instead of one. These two peaks were separated by a sharp minimum which was practically coincident with the very sharp optical absorption peak of RbI at 85°K. The results are attributed to a nonuniform distribution of *F*-centers, and to an increasingly important destruction of excitons at the surface when the optical absorption constant increases beyond 10^6 cm^{-1}.

II. EXPERIMENTAL DETAILS OF PHOTOELECTRIC MEASUREMENTS

The general technique used here in measuring photoelectric yields has been described in previous papers[3] and will not be repeated at this point. The photo-tubes were designed to permit measurements near the temperature of liquid nitrogen or air. A typical example is shown in Fig. 1. The thin films of RbI were formed by evaporating the salt from the platinum spiral (7) in Fig. 1 onto the platinized glass face (2) of the emitter structure in the photo-tube. The evaporations were completed in a few minutes at the most. The layers ranged from $<10^{-5}$ cm to 5×10^{-5} cm in thickness, as indicated by interference fringes visible against the platinum substrate. A magnet held the glass shield (5) in Fig. 1 over the hole in the collector during the evaporation to prevent possible contamination of the glass envelope (4) with RbI. As in the previous work on KI, photo-currents showed no evidence of being limited by the electrical conductivity of the salt film. Results were obtained on six separately evaporated samples in three tubes.

F-centers were made in three ways: (1) by irradiating the samples at 300°K with a narrow band of ultraviolet (of width ~ 0.02 ev) at $h\nu \sim 5.6$ ev; (2) by irradiating at 300°K with the entire output of a 10-atmos Hg arc (*AH*4) in a fused quartz envelope; (3) by bombarding the sample, of area ~ 1 cm^2, for roughly 1 sec with 1 ma of electron current at 100 v. The results were like those found previously for KI under similar treatment,[1] except that variations were somewhat larger. In different tubes, the absolute values of the photoelectric yields differed by as much as a factor of 5, and the thresholds varied by a few tenths of 1 ev. Variations for different activations of any single surface were several times less. In all cases, the features of interest in this paper were clearly reproducible.

Attempts at forming *F*-centers at 85°K by method (2) above gave spectral distributions different from those obtained when the centers were formed at 300°K. The photoelectric thresholds were roughly 0.5 ev higher, and the yields due to direct ionization rose more slowly with increasing $h\nu$. In such cases, an irreversible change occurred when the film was first warmed to 300°K. Thereafter, the behavior was quite like that for centers formed at the higher temperature. A more extensive investigation of this effect has not yet been carried out. It was assumed that the phenomenon was traceable to the diffusion processes which, according to the work of Seitz,[4] accompany *F*-center formation. All results for 85°K discussed in this paper were obtained by forming

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[1] L. Apker and E. Taft, Phys. Rev. **79**, 964 (1950).

[2] H. Fesefeldt, Z. Physik **64**, 623 (1930).

[3] See papers cited in footnote 5 of reference 1.

[4] F. Seitz, Revs. Modern Phys. **18**, 384 (1946).

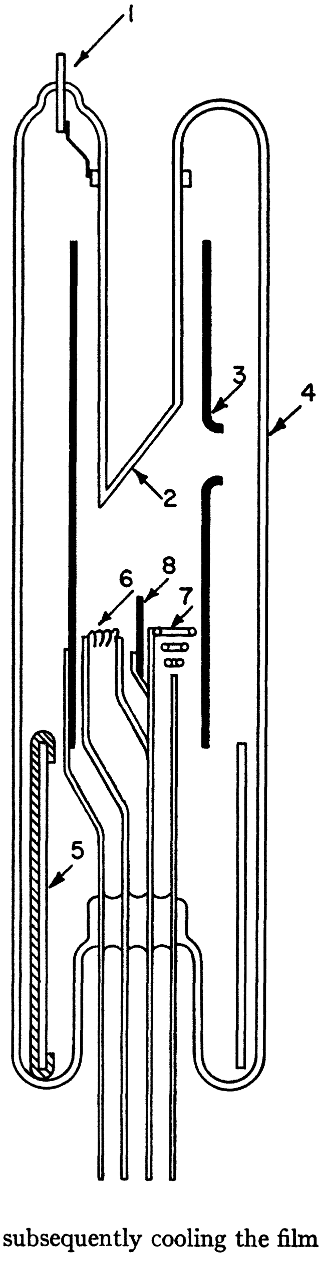

FIG. 1. Cross-section sketch of typical photocell. (1) Lead-in to platinized glass emitter (2), which can be filled with liquid nitrogen or air. (3) Stainless steel collector. (4) Corning 9741 glass envelope. (5) 9741 glass shield with nickel armature. (6) Tungsten filament electron source. (7) Platinum spiral for evaporation of RbI. (8) Shield between (6) and (7) to prevent contamination.

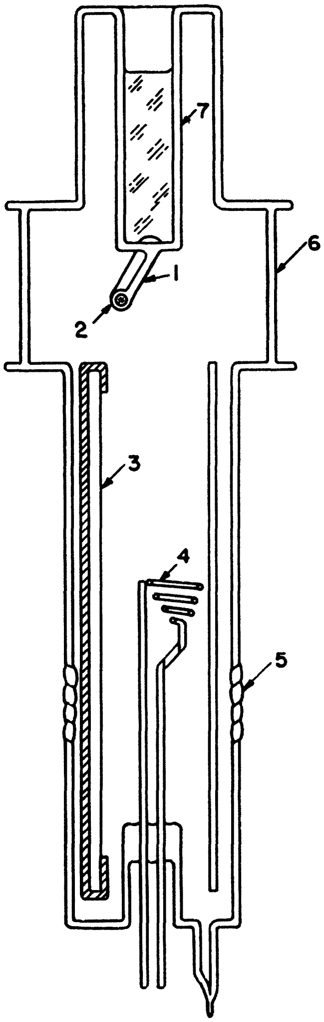

FIG. 2. Cross-section diagram of tube used for optical transmission measurements. (1) 1-mm fused quartz window attached to toroidal tube (2), which carries liquid nitrogen from the reservoir (7). (3) Glass shield with nickel armature. (4) Platinum spiral for evaporating RbI. (5) Graded seal. (6) Fused quartz window.

the centers at 300°K and subsequently cooling the film to the lower temperature.

III. EXPERIMENTAL DETAILS OF OPTICAL MEASUREMENTS

Figure 2 shows the type of tube used for optical transmission measurements. It is similar to one used by Fesefeldt[2] except that it was constructed almost entirely of fused quartz. At 85°K the thermal conductivity of this material is very low. Hence, the quartz substrate (1) for the thin RbI film was fused to a surrounding toroidal tube (2) carrying liquid nitrogen or air from the reservoir (7). The increased cross section thus available for thermal conduction prevented appreciable temperature gradients from appearing in the quartz plate when it absorbed thermal radiation from its surroundings.

The optical transmission of the system was first determined by sending a beam from a Gaertner quartz monochromator through a 0.1-cm^2 area of the quartz window (1). The transmitted radiation was detected with an Sb—Cs alloy photo-tube. RbI was then evaporated from the platinum spiral (4) onto the quartz window while the shield (3) was held in place with a magnet. After the shield was removed, the transmission measurement was repeated. No corrections were made for reflection losses. Tests on KI showed absorption peaking at 5.63 and 5.80 ev for film temperatures of 300° and 85°K, respectively, in excellent agreement with Fesefeldt's results.[2]

IV. DISCUSSION OF RESULTS

Figure 3 shows the frequency variation of the photoelectric yield from F-centers in a typical RbI sample. The concentration of centers was near the limiting value attainable by irradiation with 4×10^{11} quanta sec^{-1} cm^{-2} at $h\nu \sim 5.6$ ev (temperature, 300°K). The result is quite

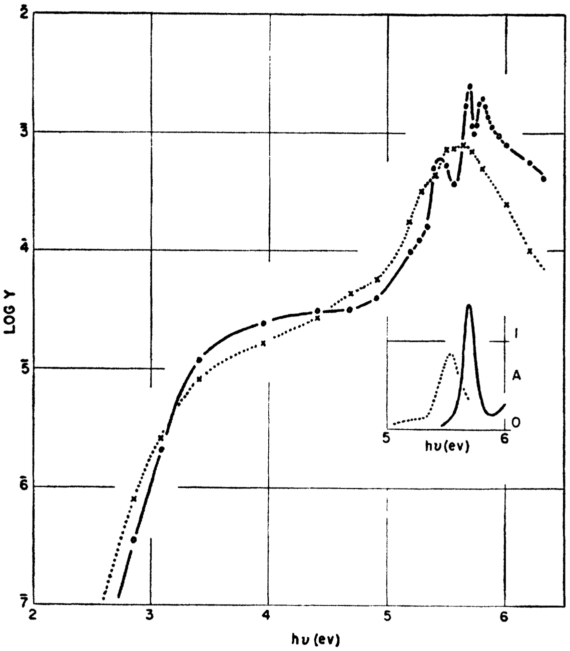

FIG. 3. Spectral distribution of the photoelectric yield Y from F-centers in RbI at 300°K (dotted curve) and at 85°K (solid curve). Y is given in electrons/quantum (note that the characteristics of the logarithms are negative). Below the photoelectric data is the optical absorption coefficient in arbitrary units on the same abscissa scale and on a linear ordinate scale.

like that previously given for KI at 300°K.[1] The peak in the photoelectric yield is not as sharp as for KI. Its location, however, is in good agreement with the peak shown by the optical absorption constant at $h\nu = 5.53$ ev.

When the film was cooled to ~85°K with liquid nitrogen or air, several changes occurred in the spectral distribution of the photoelectric yield. First, the threshold energy increased slightly, and the yield rose more rapidly with increasing $h\nu$ in this vicinity. Second, the small inflection at $h\nu \sim 5.3$ ev on the curve for 300°K shifted toward higher energies by roughly 0.15 ev and formed a separated peak. Third, the peak in the exciton-enhanced emission shifted toward higher energies and split into two clearly resolved maxima separated by a minimum near $h\nu = 5.72$ ev.

We shall consider the last of these effects first. When the temperature decreases from 300° to 85°K, the optical absorption peak shifts by about 0.15 ev, from 5.53 ev to about 5.68 ev. The exciton-induced peaks in the photoelectric yield show a like displacement. However, the peak for 300°K is flattened, and it is in the flattened region that the maximum optical absorption occurs. At 85°K, the yield curve has a contour somewhat like that of a self-reversed spectral line, and the central minimum corresponds to the optical absorption peak.[5] The flattened peak at 300°K appears to be an incipient form of this phenomenon.

Such results would be expected if the exciton-induced photoelectric yield at first rose with increasing absorption constant A, reached a maximum for an A near 10^6 cm^{-1} (the peak absorption at 300°K is known to be 7×10^5 cm^{-1}),[6] and then fell as A increased further. This would happen if the F-centers were non-uniformly distributed with a relatively low density near the surface.

In considering certain luminescence phenomena, Fano[7] has suggested that excitons are destroyed if they diffuse to a free surface. Now such a process may compete with exciton stimulation of F-centers in the RbI considered here. As the fundamental optical absorption increases from small values, the photoelectric yield at first rises because the excitons are created nearer the surface. Thus, in ionizing F-centers, they produce excited electrons in a more favorable position for escape. When the excitons are formed in a layer thinner than 10^{-6} cm, however, many may be lost by diffusion to the surface, where they are destroyed. This destruction may overshadow the tendency toward an increasing yield, and the emission accordingly may show a maximum followed by a decrease.

Hebb[8] has considered these effects in a quantitative way and has also estimated their influence on photoelectron energy distributions.

It is conceivable that the high density of excitons formed when the optical absorption is large may also be effective in limiting the yield. The number of F-centers available for ionization may be depleted. Seitz has suggested to us that excitons might be destroyed by mutual interaction. Such processes would depend on incident radiation intensity or would lead to hysteresis and irreversible changes. Explicit tests showed that the results of Fig. 3 were independent of radiation intensity over a factor of more than 10. We have therefore concluded that the effects mentioned here were not important in our samples.

We now return to the second change associated above with the cooling of the film. This concerns the inflection near $h\nu = 5.3$ ev at 300°K (and the peak near 5.45 ev at 85°K). We have seen similar effects, in varying degrees of intensity, in all of our data on the iodides of K, Rb, and Cs. The inflection, for example, is visible in the result for KI given in reference 1. Remembering that the peak absorption constants are near 10^6, one notices that the phenomenon occurs when the absorption constant reaches values of the order of 10^5. We have therefore concluded that it may be an optical effect that sets in when the transparency of the film (~10^{-5} cm thick) becomes small. Thus, radiation

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[5] There is some indication that these features in the photoelectric curves occur at $h\nu$-values a few hundredths of 1 ev higher than the optical absorption peaks. The experiments, however, may not be accurate enough to render such an observation significant.

[6] R. W. Pohl, Proc. Phys. Soc. (London) (extra part) **49**, 3 (1937).

[7] U. Fano, Phys. Rev. **58**, 544 (1940). We wish to thank F. E. Williams and Malcolm Hebb for bringing Fano's work to our attention and for helpful suggestions regarding this mechanism.

[8] Malcolm Hebb, Phys. Rev. **81**, 702 (1951).

reflected from the platinum substrate is no longer important, and the effective radiation intensity at the surface decreases by 30 percent, say, if interference effects are ignored. The photoelectric yield decreases accordingly, and an inflection or peak may result.[9] Thus, in Fig. 3, if the yields in the transparent region were lowered by an appropriate factor, this section of the curve should join smoothly to that for the opaque region. Within the experimental error in Fig. 3, a factor of two removes most of the structure even at 85°K. This factor is rather high, but it is possible that interference effects are present. While it is difficult to obtain sufficiently accurate data to be conclusive, there are indications that these inflections shift slightly, as expected, toward lower $h\nu$ when the films are made thicker.

Until more exhaustive tests are made, however, it is probably unsound to exclude the possibility that the structure arises in other ways. It is conceivable, for example, that surface impurities could produce such results in the photoelectric emission without affecting the optical absorption as measured here.

Finally, we consider the changes which occur in the low energy part of the spectral distribution when the film is cooled. The threshold increases slightly, the slope near 3 ev becomes steeper, the curvature at the "knee" increases, and the yield rises in the range from 3.3 to 4.4 ev. The relative positions of the curves in Fig. 3 are qualitatively correct, although the F-center density may have been slightly different in the two cases. Thus, in explicit tests at 3.39 ev, the yield rose and fell by 10 to 20 percent when the temperature was alternately lowered and raised five times in a total time so short that the F-center density did not change appreciably.

The increased yield at the lower temperature may be due in part to an increased free path for emerging photo-electrons, and the threshold may be affected by a temperature dependence of the electron affinity. However, an increased threshold, slope, and curvature as described above are consistent with a theory worked out by Herring[10] for photo-emission from impurities in a polar crystal. According to this viewpoint, the electrons in F-centers may be considered to occupy a band of energy states having roughly a gaussian form. The width B of this band is determined by the interaction between the F-center electron and the lattice (the Franck-Condon principle being kept in mind). In order of magnitude, B should be comparable with the width of the F-center optical absorption band, which in evaporated films is an appreciable fraction of 1 ev. The center of the gaussian band of energy states lies below the conduction band by an amount D somewhat greater than the photon energy at the middle of the optical F band. In crude fashion, the photoelectric threshold T may then be set equal to $A+D-B/2$, where A is the electron affinity. Taking $T=3$ ev, $B=1$ ev, $D>1.6$ ev, one finds that the electron affinity A is 1.9 ev or less, a theoretically reasonable value.[11]

Since the surface discussed here showed evidence of electrical non-uniformity,[12] the writers feel that a more quantitative application of Herring's work should await more extensive data.

V. SUMMARY

The results presented here show that photo-emission from F-centers in RbI at 300°K is quite like that found previously for KI. The work thus furnishes additional evidence for exciton-induced photo-emission. A new effect found near 85°K shows that the efficiency of this process at first increases with increasing optical absorption, reaches a maximum of more than 10^{-3} electron/quantum for an absorption constant near 10^6 cm^{-1}, and then decreases. This result may be explained qualitatively by a non-uniform distribution of F-centers, and by Fano's hypothesis that excitons are destroyed when they diffuse to a free surface. Hebb has derived interesting information in a quantitative analysis of the effect. A minor variation on the low energy side of the exciton-induced peak in the photoelectric yield is attributed to the onset of opacity in the thin salt film. The temperature variation of the yield due to direct ionization is described. Satisfactory qualitative agreement was obtained with Herring's analysis of photo-emission from impurities in polar crystals.

The effects treated above are, of course, not restricted to RbI. Attention was confined to this substance here because data on it were most complete. The same type of phenomena appeared with KI, KI doped with Tl, and CsI.

We are indebted by Frederick Seitz, Harvey Brooks, and Malcolm Hebb for valuable discussions of theoretical questions. Jean Dickey has given us her generous help throughout the experiments.

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[9] For a related effect, see E. A. Taft and J. E. Dickey, Phys. Rev. 79, 625 (1950). H. B. DeVore has informed us that he has observed a similar phenomenon in BaO. Thick layers of KI heavily doped with Tl show a like decrease in yield at the edge of the Tl absorption band.

[10] C. Herring, Phys. Rev. 73, 1238 (1948).

[11] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chapter 11; N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1940), p. 97.

[12] As a function of applied voltage, the photo-current increased five to eight times more rapidly than that from a uniform metal. See also reference 1.