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Energy Distribution of External Photoelectrons from *F*-Centers in RbI

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Energy distributions of the external photoelectrons from *F*-centers in RbI were determined by retarding-potential techniques. Precautions were taken to secure electrically uniform surfaces. The photoelectrons then emerged in two separable groups. The first, termed the *f*-group, was composed of relatively fast electrons that were attributed to direct photon ionization of *F*-centers. Photoelectron energies were distributed in a band, roughly gaussian in form, that was treated according to a theory given by Herring. The Franck-Condon principle was taken into account; scattering of excited electrons was neglected. The second group of photoelectrons, termed the *s*-group, was comparatively slow. The energy distribution had an unusual form and peaked at the surprisingly low value of 0.3 or 0.4 ev, independent of $h\nu$. Exciton-enhanced emission was almost entirely of this type. Three factors that may influence the *s*-type distribution are mentioned: Hebb's calculations indicate that lattice scattering of exciton-induced emission may be important because of the relatively large depth of origin of these photoelectrons. As suggested by Seitz, degradation of exciton energy prior to *F*-center stimulation may be involved. Finally, some of the photoelectrons in the *s*-group may arise in other types of centers.

I. INTRODUCTION

PREVIOUS reports have treated the frequency variation of the exciton-enhanced photoelectric emission from *F*-centers in alkali iodides.[1] Energy distribution data, giving additional information on the processes involved, are reported here for RbI. The results show that the photoelectrons emerge in two distinct energy groups. The first group consists of relatively fast electrons. Apparently, they arise by direct photon ionization of *F*-centers. Their energy distribution is treated here by a method due to Herring. The Franck-Condon principle is taken into account, but the scattering of excited electrons is neglected since it does not appear to change the main features of the distribution.

The second group consists mainly of slow photoelectrons. They have an unusual energy distribution, approximately exponential in character. Exciton-enhanced emission consists almost entirely of this type. The energy distribution is not as easily interpreted as that for the first group, and this paper discusses it only in qualitative fashion. Three factors mentioned are lattice scattering of exciton-induced emission as calculated by Hebb, degradation of exciton energy as suggested by Seitz, and ejection of photoelectrons from initial states in other types of centers.

II. TREATMENT OF THE EMITTERS

The general technique and the phototubes used in this work have been described in (I).[1] Five evaporated RbI films (in two tubes) were studied in detail; they ranged from 10^{-5} to 10^{-3} cm in thickness. The *F*-centers were produced by three methods given in (II): (1) irradiation with monochromatic ultraviolet of known intensity; (2) flooding with a broad band of ultraviolet overlying the first fundamental absorption band of RbI; (3) electron bombardment for several seconds at current densities varying from 2 μa/cm^2 at 25 v to 1 ma/cm^2 at 500 v. Results were reproducible under these different conditions except that the equilibrium concentration of *F*-centers (as indicated by photoelectric yields) varied by a factor of 2 or 3.

Retarding-potential measurements impose more stringent requirements on surface uniformity than do the yield determinations reported in (I) and (II). Although RbI seemed much more tractable in this respect than KI, non-uniform surfaces, nevertheless, occurred in most cases. Current-voltage characteristics then failed to show clear-cut saturation points, indicating that relatively large scale patch structures were present. (For the samples discussed in (I) and (II), this condition was always evident, but it was of no serious importance.) These patches often appeared after several activations with ultraviolet irradiation, but electron bombardment sometimes eliminated them. In spite of time-consuming difficulties from this source, uniform surfaces were finally produced by all three of the methods mentioned above. Only such surfaces are discussed in this report. Twenty separate successful activations were carried out on the samples considered here.

The chemical constitution of the samples is a particularly important variable in this type of work. It is not very easy to determine or to control. Evaporation of a salt like RbI in a sealed-off, gettered vacuum obviously does not constitute a definite chemical situation. Experiments in auxiliary tubes showed, for example, that the following process may occur: When the source material is heated, it may lose a very small amount of I. It thereby acquires a corresponding amount of excess Rb in the form of permanent *F*-centers or more complicated aggregates. The concentration of these may be high enough to color the salt. A transient pressure of free I thus may build up during the deposition of the sample. This has its greatest effect, naturally, on the part of the RbI that deposits last. If it persists appreciably after the evaporation ceases, it may continue to react with the outer layers of the material already deposited.

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[1] L. Apker and E. Taft, Phys. Rev. **79**, 964 (1950); **81**, 698 (1951)—hereafter denoted in the text by (I) and (II), respectively. M. Hebb, Phys. Rev. **81**, 702 (1951).

We do not understand this process in any complete detail. It is clear, however, that the spatial distribution of I ion vacancies and their number may be greatly affected. The pronounced "self-reversal" effect exhibited by the exciton-induced photoelectric yield from RbI in (II) was doubtless influenced by this phenomenon. A sparsity of F-centers near the sample surfaces could easily have arisen, particularly since the tubes used in this earlier work were of relatively small volume. Thus, "dead layers" 140A thick were found by Hebb[1] in his quantitative treatment of these previous data. They probably originated largely in an F-center sparsity.

One way to minimize this difficulty (or at least to obtain *different* difficulties) is to evaporate the RbI in a very low pressure of Rb vapor. This we have done in the present work. A glass pellet of Rb metal was incorporated in a side arm on the evaporation chamber of the second phototube. This pellet was broken before the tube was sealed off. The vapor pressure of Rb at 300°K is roughly 10^{-7} mm Hg. Samples were deposited and investigated in the presence of this vapor, which could be frozen out with liquid nitrogen if desired.

The photoelectric yields, at the exciton-induced peak near $h\nu = 5.56$ ev, amounted to as much as 0.04 electron/quantum under these conditions. Auxiliary tubes like those in (II) showed that the "self-reversal" effect at 85°K was either very small or even absent. In agreement with this, the "dead layer" thickness estimated by Hebb's method had an upper limit much smaller than the 140A above. It is even conceivable, of course, that the F-center concentration was non-uniform and relatively high near the surfaces of these samples. At any rate, the situation represents an opposite extreme from that in (II).

For purposes of comparison, the Rb pellet was omitted from the first phototube used in the present work. The photoelectric yields at the exciton-induced peaks were roughly 8×10^{-3} electron/quantum. Hebb's[1] calculations indicate that the "dead layer" thickness for these samples was 80A or less. Energy distribution data were not significantly different in form from those determined with the second tube, and they are therefore used in this paper.

Other details are mentioned where pertinent in succeeding sections.

III. EMITTER "WORK FUNCTIONS"

Figure 1 shows typical current-voltage characteristics for an RbI emitter containing F-centers made by irradiation near $h\nu = 5.56$ ev. In all cases, the concentration of centers was close to the limiting value attainable with 4×10^{11} quanta sec^{-1} cm^{-2} incident on the surface at 300°K. (The activation curve was practically the same as that for KI in reference 1. It will not be repeated here.) Values of the parameter V_0, "the stopping potential for an ideal metal at 0°K," are marked for the various values of $h\nu$ in question.[2] The collector work function is $\varphi_c = h\nu + eV_0 = 4.8$ ev. The saturation point V_s, which determines the condition of zero field between emitter and collector, is indicated at +0.3 v.

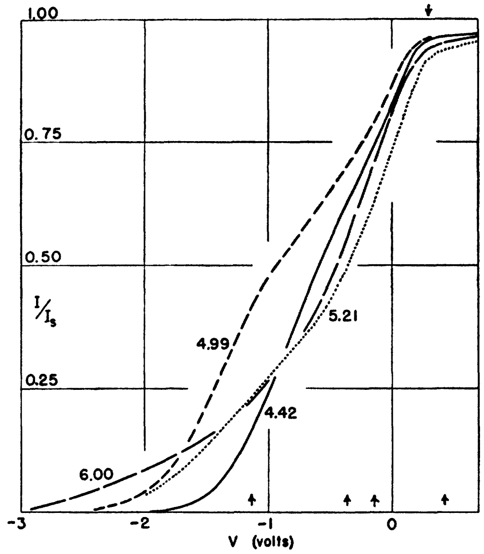

FIG. 1. Typical current-voltage characteristics for RbI. Arrow at the top marks V_s. From left to right at the bottom, arrows mark values of V_0 for decreasing values of $h\nu$ as indicated by numbers next to the corresponding curves. Curves are normalized with $I/I_s = 1.0$ at $V = 10$ v.

We note that the RbI is not in an equilibrium state during these photoelectric measurements. The F-centers and V-centers[3] are metastable. The electric current in the sample may be carried by both electrons and ions. The potential just outside the surface therefore may not be fixed by an ordinary Fermi level for the electrons in the occupied states from which the photoelectrons are ejected. In extreme cases, involving film thicknesses greater than those used here, there may not be enough conductivity of any kind to replace the charge carried away by the photoelectrons. A significant voltage may then appear across the RbI layer, and the surface may not reach a steady potential for several minutes. It is thus clear that V_s may not have the same connotation as it does when thermal and electrical equilibrium exists.

Under these conditions, precautions are obviously necessary in coming to meaningful conclusions. The following points were noted here: Current-voltage characteristics were independent of incident radiation intensity over at least a factor of ten.[4] As shown in Fig. 1, V_s did not depend on $h\nu$ and thus was normal in behavior. At collecting fields near 1000 v cm^{-1}, currents were about 4 percent larger than at 10 v cm^{-1}. This rate of increase is comparable with that for the common metals in the auxiliary emitters used to determine V_0.

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[2] See (I), reference 5, for details of the experimental technique.

[3] F. Seitz, Phys. Rev. **79**, 529 (1950); see also (I), reference 4; E. Burstein and J. J. Oberly, Phys. Rev. **79**, 903 (1950).

[4] It was possible to distort the characteristics by using radiation intensities an order of magnitude or more in excess of those discussed here.

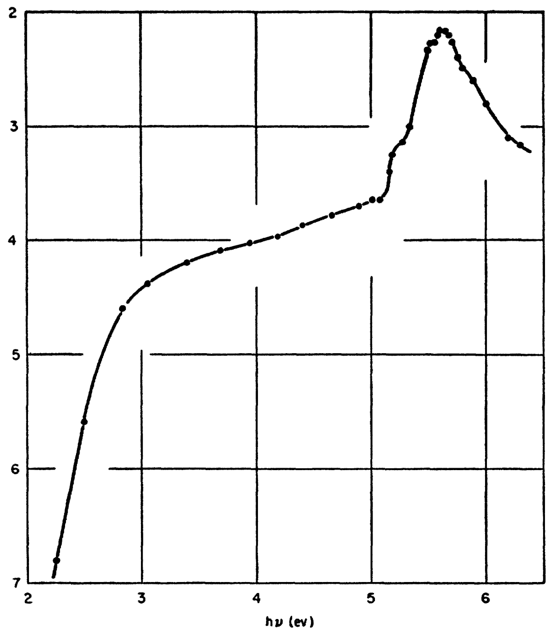

FIG. 2. Spectral distribution of photoelectric yield Y in electrons/quantum for the sample of Fig. 1.

We believe, therefore, that patch structures were not serious enough to affect the conclusions in this paper. As mentioned in (I) and (II), photocurrents were proportional to radiation intensity. A steady state was always observed, and it must have been reached within two seconds after the incidence of the radiation. We conclude that there was no important voltage drop in the emitters and proceed to treat the currents in the manner customary for ordinary photoelectric emission.

Returning to Fig. 1, we take $V_s = 0.3$ v. Thus, the electric field outside the RbI is the same as would be found outside a good electronic conductor with a work function $\varphi = \varphi_c - eV_s = 4.5$ ev. For an equilibrium case, the Fermi level for the electrons in the occupied energy states would thus lie 4.5 ev below the vacuum potential just outside the surface barrier. This Fermi level would coincide with that in the metal substrate on which the RbI film was deposited.[5] Electrons from energy levels more than 0.2 ev above it would not be detected in practice, the population probability for such states being less than 5×10^{-4} at 300°K. Hence, no current would be observed at room temperature for applied potentials 0.2 v more negative than V_0.

Clearly, this type of argument cannot apply to the data for RbI in Fig. 1. Currents are observed for applied potentials more negative than V_0 by over 1 v. The current-voltage characteristics do not approach zero in the exponential way typical of a Fermi distribution of electrons in fixed, one-electron energy levels.

We take the following viewpoint in discussing this situation: Although there is apparently no genuine electronic equilibrium between the RbI and its surroundings, the definite saturation point V_s shows that the salt behaves as though it had a definite work function. We shall call this quantity φ'', using the primes to distinguish it from the work function of an emitter in true equilibrium. We associate with φ'' a fictitious "Fermi level" μ'' that may be found unambiguously from the data in Fig. 1.

Samples of KI investigated in parallel fashion have shown values of φ'' which decreased from about 4 ev to 2.5 ev in the course of an extended series of measurements. The current-voltage characteristics retained their form, however, merely shifting bodily toward more positive values of V. This is quite like the behavior observed when a true Fermi level rises in the forbidden energy band of an ordinary semiconductor in true equilibrium. We prefer to leave further consideration of this point entirely open here, since the topic appears to need more experimental study than it was accorded in this work.

IV. ENERGY DISTRIBUTIONS

Differentiating characteristics like those in Fig. 1 and using the spectral distribution of Fig. 2, we obtain the energy distributions in Figs. 3 and 4. In Fig. 3, one notices that the photoelectrons emerge in two groups. The first we shall call the *f*-group, since it is faster than

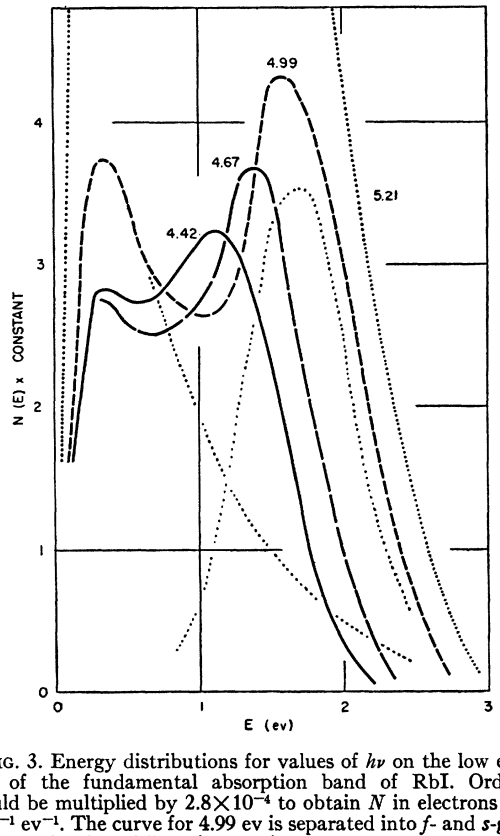

FIG. 3. Energy distributions for values of $h\nu$ on the low energy side of the fundamental absorption band of RbI. Ordinates should be multiplied by 2.8×10^{-4} to obtain N in electrons quantum^{-1} ev^{-1}. The curve for 4.99 ev is separated into *f*- and *s*-groups as shown by dotted lines (see text).

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[5] We avoid discussing possible complications due to barrier layers comparable in thickness to the sample.

the second. It produces clear-cut high energy peaks in Fig. 3. (That near $E=1.6$ ev on the curve for $h\nu=4.99$ ev is an example.)

Now, the precision of this type of measurement on such intractable materials is obviously limited. Errors of the order of 10 percent may easily appear in these distributions. Thus, the locations of these f-peaks may be uncertain within, say, 0.1 or 0.2 ev. (An idea of these errors may be gained by observing that the high energy tail for $h\nu=4.67$ ev seems to lie too close to that for 4.42 ev.) We consider it significant, however, that the f-group peak progresses linearly toward higher energy with increasing $h\nu$. Thus, these photoelectrons behave as though ejected in normal fashion from a rather narrow band of ordinary electron energy levels, the excitation probability varying only slowly with $h\nu$. In contrast, this type of description does not appear useful for the other group of photoelectrons; it would lead to a density of initial states that decreases exponentially with increasing energy and to an excitation probability that changes violently with $h\nu$.

We have proceeded, tentatively, by attributing the f-group to direct ionization of F-centers and shall discuss the mechanism in more detail later.[6] We have assumed that the f-type energy distribution is symmetrical (similar to a gaussian distribution, for example). In this way, it is possible to isolate it crudely from the other group of electrons, which does not affect it greatly in the region of high energies (Fig. 3).

The slow, second group we shall term the s-group. As seen in Fig. 3, it produces the peaks near $E=0.3$ ev. In the separation process mentioned above, this s-group maximum is practically undisturbed, since the f-group makes only a small contribution to the composite distribution in this region of low energy. Toward higher energies, the derived s-type distribution falls off roughly along an exponential at a rate near one decade per 1.8 ev.

This s-group energy distribution is unusual in form and is peaked at a surprisingly low energy. The phenomenon appears to be characteristic of exciton-induced emission. Thus, the f-group predominates for $h\nu<5$ ev, where exciton production is small. When exciton stimulation and direct ionization become comparable, as at $h\nu=5$ ev, the photoelectrons emerge in the two clearly separable f- and s-groups of comparable magnitude. Above 5 ev, exciton stimulation increases greatly; the additional current appears almost entirely in the s-group. In the same region, the f-group is practically unchanged (even below 5 ev, the f-peak increases in height no more rapidly than the first power of $(h\nu-3.3$ ev$)$). Thus, it is practically undetectable at $h\nu=5.56$ ev in the presence of an s-group 50 times larger (Fig. 4).

This suggests that the f- and s-groups of photoelectrons arise by direct ionization and by exciton stimulation, respectively, in these experiments. We shall take this point of view in this paper. We should point out, however, that work now in progress on RbBr indicates that distributions similar to those of the s-group may arise well outside of the fundamental absorption band if more permanent centers (perhaps associated with impurities or with aggregates of F-centers) are present. Phenomena other than simple exciton stimulation of F-centers, therefore, appear capable of producing energy distributions of this same general character.

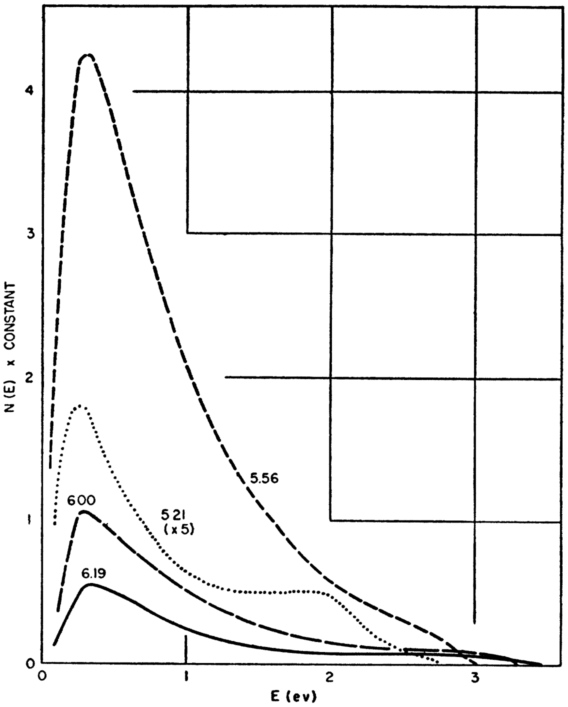

FIG. 4. Energy distributions for values of $h\nu$ in the fundamental absorption band. Ordinates should be multiplied by 2.8×10^{-3} for $h\nu=5.21$ ev and by 1.4×10^{-2} for the other three values. Thus, the curves are actually 10 and 50 times higher, respectively, than those in Fig. 3.

As discussed below in Sec. V, a theory worked out by Herring[6] affords an attractive simple explanation of the f-group. In contrast, the exciton-induced s-group appears to be more complex, and a definite interpretation will not be attempted here. For the sake of completeness, however, we shall mention factors that may be involved and that depend on further theoretical work for satisfactory comparison with experiment.

Several independent mechanisms may tend to produce slow electrons like those in the s-group. One is lattice scattering of excited electrons during their migration to the surface. This phenomenon has been treated quantitatively by Hebb,[1] who has arrived at a distribution quite similar to that given here for $h\nu=5.56$ ev. The "dead layer" thickness characteristic of this sample was estimated to be 80A or less.

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[6] C. Herring, Phys. Rev. **73**, 1238T (1948), has given a theory of this type of emission (in the absence of scattering) in another connection; the treatment in Sec. V is based on his work.

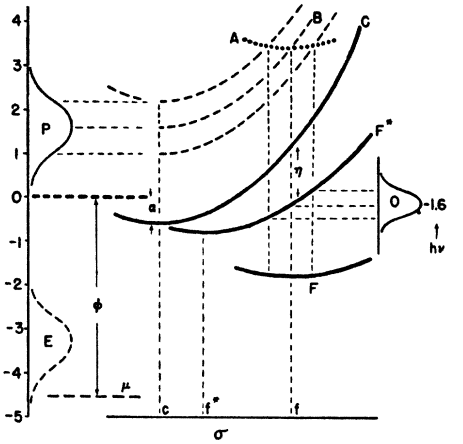

Fig. 5. Schematic diagram (after Herring) illustrating direct ionization of *F*-centers in RbI for $h\nu=4.99$ ev. The abscissa σ is a configurational parameter of the familiar type; in this case it might be the distance between negative ions adjacent to the *F*-center. The energy scale at the left is in electron volts; it applies directly to all curves except *O*, where the scale of $h\nu$ on the right should be used. The abscissas for the auxiliary curves are as follows: *O*, absorption in the optical *F*-band as a function of $h\nu$; *P*, energy distribution of photoelectrons in the *f*-group as a function of kinetic energy; *E*, apparent density of levels for electrons in *F*-centers as a function of energy relative to the top of the surface barrier. The energy curves *B*, *C*, *F*, etc. are for illustrative purposes and have only semiquantitative significance (see reference 10, p. 136).

In order to avoid a similar effect on the *f*-group, we must assume that these electrons arise closer to the surface. This would happen if excitons were destroyed at surfaces, as suggested by Fano.[7] From this point of view, the separability of the *f*- and *s*-groups constitutes evidence for Fano's hypothesis, and the 80A "dead layer" derived by Hebb for this sample must be attributed primarily to this phenomenon.

Another effect which would produce relatively slow electrons has been suggested by Seitz,[8] namely, degradation of exciton energy before *F*-center stimulation. This would be particularly probable if the excitons were not mobile but instead interacted with *F*-centers in a process like that considered by Foerster.[9] Energy would then be dissipated by lattice polarization after exciton formation. Another possibility involves selection rules that limit the optical transition to a state at the top, rather than at the bottom, of the exciton energy band. Then excitons could be degraded by inelastic scattering during migration to *F*-centers. If only processes like these are important, it is not necessary to invoke surface destruction of excitons, of course, in explaining the differences between *f*- and *s*-groups.

A third factor that may be partially responsible for the *s*-group is the ejection of photoelectrons from more complicated initial states such as may arise from impurities or aggregates of *F*-centers. These aggregates may form when *F*-centers are bleached with light in their absorption band or when they decay because of thermal agitation. They are more permanent than *F*-centers and have higher photoelectric threshold energies. It is difficult to avoid small concentrations of such centers. They may well account for the slight rise in the photoelectric yield between 4 and 5 ev in Fig. 2.

One notes that a complete explanation of the effects reported here must account for energy losses of the order of magnitude 1 ev for that part of the *s*-group arising in *F*-centers. In particular, quanta of energy 5.6 ev are required to form excitons at the peak of the fundamental absorption band. However, the energies of the photoelectrons produced are, in the main, no greater than those ejected by direct ionization due to quanta of energy between 4 and 5 ev. These large losses and the unusual energy distribution associated with the *s*-group are in obvious contrast with the apparently simple behavior of the *f*-group.

V. ORIGIN OF THE *f*-GROUP

Figure 5 is a schematic diagram patterned after one used by Herring[6] to describe photoelectric emission from an impurity level in an ionic semiconductor. The abscissa is a configurational parameter σ describing qualitatively the position of ions in the distorted lattice near an *F*-center. The ordinate is the total energy of the *F*-center system. In the customary way, this total energy is considered to be distributed between the *F*-center electron and the ions in the lattice around it. Initially, the electron is in the state *F* in Fig. 4. At 300°K, σ vibrates about an equilibrium value *f*, and the various configurations assumed by the center have a Boltzmann distribution in energy. If we approximate *F* by a parabola, they have a gaussian distribution in σ.

Quanta, of 5-ev energy in Fig. 5, excite electrons from the state *F* to a group of levels lying along the dotted curve *A* in the conduction band of the crystal. According to a strict interpretation of the Franck-Condon principle, the curve *A* lies directly above *F* and is parallel to it. It represents total energy distributed among a free electron in the conduction band and ions in the distorted lattice around the vacancy which was formerly an *F*-center. When the lattice relaxes to the configuration *c*, the equilibrium position for a vacancy, the released energy (of the order of 1 ev) is carried away by the lattice vibrations. The kinetic energies of the electrons are measured by their positions above the bottom *C* of the conduction band. (The other curves, *B* for example, are parallel to *C*.) It is evident that the distribution of kinetic energies is similar to a gaussian distribution in character. The half-width of the band should be of the order of 1 ev, and it should vary with the square root of the tempera-

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[7] U. Fano, Phys. Rev. 58, 544 (1940).

[8] Frederick Seitz, private communication; *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Secs. 96, 108, 148; *Pittsburgh Symposium on Plastic Deformation of Crystalline Solids* (Naval Research Laboratory).

[9] T. Foerster, Ann. Physik 2, 55 (1948).

ture.[10] For purposes of comparison, the analogous behavior of the absorption in the optical F-band is indicated in the familiar way.[10]

Some of the excited electrons escape over the barrier at the crystal surface and emerge with a band of kinetic energies, P in Fig. 5, which is similar to the corresponding band inside the surface. The average kinetic energy is lower, of course, and the distribution is distorted by the decrease of the escape probability with decreasing energy.[2] In experiments like those described here, it is doubtful that the distortions can be detected. When viewed against a background like that due to the s-group, this distribution would thus appear as a partially resolved peak similar to a gaussian distribution. Thus, we correlate it directly with the f-group of photoelectrons found in these experiments. For $h\nu = 4.99$ ev, the center of the band lies about 1.7 ev above the zero level. Thus, the photoelectrons appear to have come from a similar band E centered roughly 3.3 ev below the surface barrier.

Let us say for the moment that the F^* level, the excited state of an F-center, lies below C by an amount η, for the configuration $\sigma = f$. Then the electron affinity (α in Fig. 5) of RbI becomes $\alpha = 4.99 - 1.6 - 1.7 - \eta = 1.7 - \eta$ ev, since the center of the band P is at 1.7 ev for $h\nu = 4.99$ ev, and the center of the optical absorption band 0 is at $h\nu = 1.6$ ev. In Fig. 5, η is taken for purposes of illustration to be near 1 ev; thus, α is 0.7 ev, consistent with the upper limit of 1.9 ev obtained in (II).

The spectral distribution[6] in Fig. 2 is also in qualitative agreement with that expected on the basis of Herring's work. It indicates that the center of the band E in Fig. 5 lies below the vacuum level by about 3 ev, a value slightly smaller than was obtained above. The discrepancy may not be significant in view of our experimental uncertainties (especially in the energy distributions). It would not be surprising, however, to find that the scattering neglected in this treatment could shift the F peaks in Figs. 3 and 4 by this amount without obliterating the main features of the distributions.

It will be noted that the "Fermi level" μ'', determined from the V_0 values in Fig. 1, lies well below the F-center energy levels E in Fig. 5. This is consistent, of course, with the point of view taken in Sec. III.

VI. CONCLUDING REMARKS

The salient point discussed above is the striking difference between the energy distributions of the f- and s-groups of photoelectrons. The separability of these groups was a fortunate circumstance. Such a separation cannot always be effected. As mentioned before, the pronounced tendency of the alkali iodides to exhibit non-uniform surfaces is a serious hindrance. A more fundamental consideration involves the electronic energy structure of the emitter; if a separation is to be convincing, the energy at the f-group peak must reach values of 1 or 2 ev before exciton-induced emission becomes important. (From this point of view, the iodides present a less favorable case than bromides, for example.)

In parallel work on KI, results were less clear-cut than those given here. Using the behavior of RbI as a guide, however, we have convinced ourselves that the same phenomena appear.

It is a pleasure to record our thanks to Malcolm Hebb for many stimulating conversations. To Harvey Brooks, we are grateful for helpful discussions, especially regarding the energy distributions; and to Frederick Seitz we are indebted for many suggestions regarding exciton behavior. Jean Dickey has given us her generous help in the phototube design.

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[10] See, for example, N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1940), chapter IV. Zero point vibrations are neglected here.