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Intrinsic Photoconductivity in the Alkali Halides*

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Photoconductivity in thin films of RbI, KBr, and KCl has been measured at temperatures of 10 and 80°K in the spectral range from 5.5 to 10 eV. The *Schubweg* of the photoelectrons and the yield of photoelectrons per incident quantum were determined. In the case of RbI the data tend to confirm the existence of exciton states lying between the two components of the familiar spin-orbit doublet, as was recently suggested by Fischer and Hilsch. It is estimated that the band gaps of RbI, KBr, and KCl are 6.37, 8.0, and 8.7 eV, respectively.

INTRODUCTION

THE internal photoelectric effect has been investigated in the alkali halides by several[1-4] workers. Measurements of intrinsic photoconductivity have been carried out primarily to determine the optical band gap of these materials and to provide information about the nature of the relatively sharp absorption bands, commonly called exciton bands, found on the low-energy side of the fundamental absorption of the alkali halides.[5] The results of these experiments have been reported in terms of the photocurrent per incident photon and they have been carried out only at temperatures above the boiling point of liquid nitrogen. In the present work the photocurrents were measured in thin films of RbI, KCl, and KBr. Saturation of the currents as a function of electric field was achieved so that the actual *Schubweg* of the photoelectrons could be determined. In addition, measurements were made of the yield for photoelectrons per incident quantum and the experiments were carried out at temperatures as low as 10°K.

In the absorption spectra of all the alkali halides two strong lines appear which have been associated with transitions from the p^6 ground-state configuration of the halide ions to an excited-state configuration p^5s.[5,6] In addition to this so-called spin-orbit doublet, a much weaker band resembling a step appears in the spectra of these salts.[5] This step has been associated with band-to-band transitions, and the optical band gap is usually given as the energy of the leading edge of the step.[7] Recently, Fischer and Hilsch[8] have observed that structure occurs on this step if care is taken to produce well-annealed relatively thick films. The structure is most pronounced in RbI. Figures 1 and 2 illustrate these facts. Here the optical absorption spectrum of a thin film of RbI is shown at 80°K and 10°K. The film was too thick to permit the optical absorption in the peaks of the halogen-ion doublet to be measured. The positions of the components of the doublet are indicated by arrows in Figs. 1 and 2. Attention is directed to the region between the components of the doublet, where the structure found by Fischer and Hilsch[8] appears. According to these workers, the small band at 6.12 eV, seen in the spectrum at 10°K, represents the first excited state of an exciton, whose ground state is represented by the first component of the doublet. The band at 6.25 eV may be due to higher

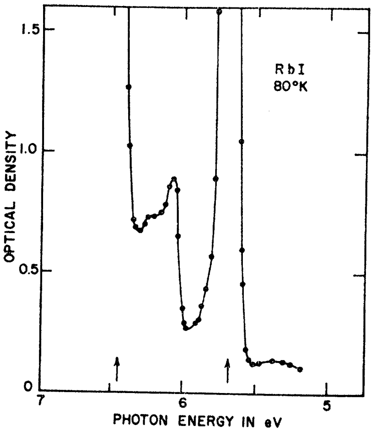

FIG. 1. Optical absorption spectrum of RbI at 80°K (after Baldini).

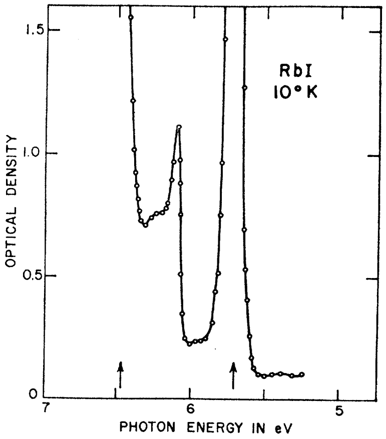

FIG. 2. Optical absorption spectrum of RbI at 10°K (after Baldini).

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[1] J. N. Ferguson, Phys. Rev. **66**, 220 (1944).

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[6] R. S. Knox and N. Inchauspe, Phys. Rev. **116**, 1093 (1959).

[7] J. C. Phillips, Phys. Rev. **136**, A1705 (1964).

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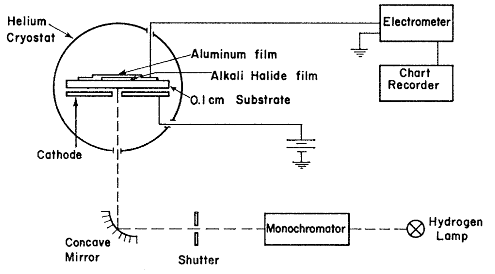

FIG. 3. Schematic diagram of experimental arrangement.

excited states of the same exciton. The structure is thus explained in terms of the Wannier-Mott or hydrogenic exciton model,[9] rather than the Frenkel model[9] which has usually been applied to these materials. If these are exciton lines, the true optical band gap of RbI should lie at the limit of the series of lines rather than at the leading edge of the "step." The measurements on photoconductivity discussed in this paper were carried out in part to check the validity of these ideas.

EXPERIMENTAL PROCEDURE

The alkali halides used, with the exception of KCl, were grown by Dr. Karl Korth of Keil, Germany, by the Kyropolos method. The KCl was obtained from the Harshaw Chemical Company. Samples in the form of thin films were evaporated on LiF or fused silica substrates at room temperature with an aluminum film evaporated over the alkali halide. No attempt was made to anneal the films at higher temperatures. In this manner, a sandwiched sample configuration was formed. The sample was mounted in a helium cryostat to maintain a low temperature for the period of time necessary to perform the experiment, and a calibrated Au:Co—Ag:Au thermocouple was used to measure the temperature. A clean vacuum was obtained by evacuating the cryostat with an ion-getting pump to pressures always below 10^{-7} Torr.

A schematic diagram of the experimental arrangement used for the measurement of photoconductivity is shown in Fig. 3. Ultraviolet radiation was incident on the alkali halide film after passing through a slit in the center of a brass disc, which served as the cathode, and through the LiF or fused silica substrate. The field was developed by applying a voltage to the cathode from a highly insulated battery supply. The aluminum film backing the alkali halide served as an anode and was connected to the input of a vibrating-reed electrometer. The output was recorded by a strip-chart recording potentiometer. By careful design and construction a guarded circuit configuration was maintained.

The light from a concave grating monochromator was focused on the sample with a spherical concave mirror. A 931A photomultiplier in conjunction with a sodium salicylate phosphor was used to monitor the intensity of the ultraviolet radiation on the sample. An absolute measure of the light intensity was obtained with an EMI 6097S photomultiplier–sodium salicylate combination which was calibrated using a thermocouple as a secondary standard.

Spectral-response measurements of the materials were taken at liquid-nitrogen and liquid-helium temperatures. The slit width of the monochromator was 0.95 mm corresponding to a band pass of 38 Å. Measurements were made with an Applied Physics Lab vibrating-reed electrometer using the constant deflection method in cases where the signal exceeded 10^{-5} A. The rate-of-change method was used for currents less than this. Care was taken to avoid polarizing the crystals during the measurements. It was found that the photocurrents varied linearly with the intensity of the stimulating radiation over the range of intensities used in these experiments.

The thickness of each film was determined by placing an optical flat over the aluminized sample and measuring the fringe shift in the Fizean fringes. The displacement of the fringes could be measured to about $\frac{1}{10}$ of a fringe or $\frac{1}{12}$ of a wavelength. Film thicknesses ranging between 680 and 9020 Å were used.

Care was also taken to be sure that photoemission did not contribute to the measured currents. The electrode arrangement and direction of illumination, as described above, were such as to make photoemission from the alkali halide unlikely. Furthermore, the voltage at which saturation of the current became observable was always a linear function of the film thickness, implying that the current measured was caused by an internal photoelectric effect. To further demonstrate this fact, a thin crystal of RbI about 0.1 mm thick was used with the same electrode geometry as the films. The currents in the crystal were linear with applied field over the range of fields normally

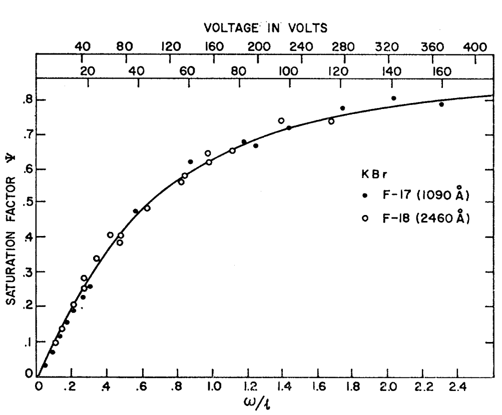

FIG. 4. Saturation curves for KBr at 80°K. The upper scale of the applied voltage applies to film F-18, and the lower scale to film F-17.

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[9] For a review of exciton models see R. S. Knox, Solid State Physics Suppl. 5 (Academic Press Inc., New York, 1963).

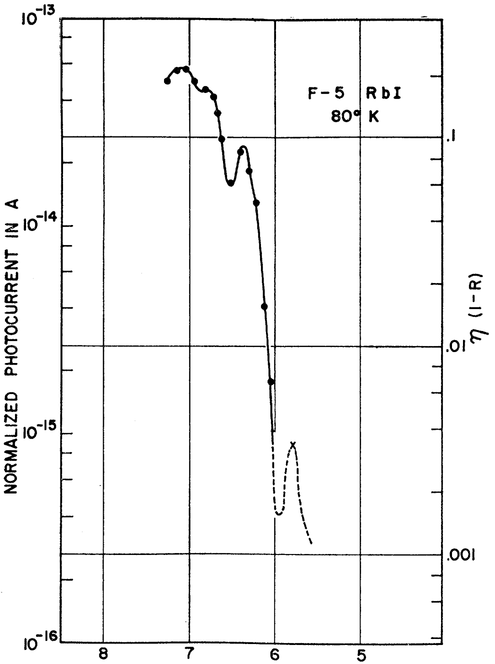

FIG. 5. Spectral response of RbI at 80°K.

used. Saturation began in the crystal only when fields in excess of 5×10^4 V/cm were employed. Other tests were also used to make sure that photoemission did not play a role in measurements.

DISCUSSION OF RESULTS

A. Measurements of the *Schubweg* and the Yield for Photoelectrons

In regions where the absorption coefficient is large enough compared to the reciprocal of the sample thickness, the photocurrent in the sample is given by the expression

$$i=e\eta N_0(1-R)\psi, \tag{1}$$

where e is the electronic charge, η is the quantum efficiency, R is the reflectivity, N_0 is the number of incident photons per second and ψ, the saturation factor, is given by a formula due to Hecht[10]:

$$\psi=(\omega/l)(1-e^{-l/\omega}), \tag{2}$$

where l is the sample thickness. In the latter expression ω, the *Schubweg* is assumed to be linearly related to the field, the constant of proportionality being called the *Schubweg* per unit field. That is:

$$\omega=\omega_0E, \quad \text{or} \quad \omega=\omega_0V/d_{\text{eff}}, \tag{3}$$

where ω_0 is the *Schubweg* per unit field, V is the voltage and d_{eff} is the effective separation of the electrodes. The latter quantity is defined by:

$$d_{\text{eff}}=l+(\epsilon_f/\epsilon_s)d, \tag{4}$$

TABLE I. The *Schubweg* per unit field, for RbI, KBr, and KCl at 80°K. The excitation energy at which the *Schubweg* was measured is shown. The quantum yield per incident photon is also given.

Sample	Excitation energy (eV)	η $(1-R)$	ω_0 (cm²/V)
RbI	6.5	0.06	2.69×10^{-8}
KBr	8.6	0.11	1.31×10^{-8}
KCl	8.6	0.03	2.00×10^{-7}

where l and ϵ_f are the sample thickness and dielectric constant, and ϵ_s and d are the dielectric constant and thickness of the substrate.

The above expressions were used to determine the *Schubweg* per unit field, by fitting the measured values of the photocurrent as a function of field to the theoretical expression (2). An independent measurement of the photon flux was then used to determine $\eta(1-R)$ from expression (1), for a given value of the field. Measurements were made at a photon energy where the absorption coefficient was large enough to make the approximation mentioned above valid. Data were obtained on two different sample thicknesses for each alkali halide. A typical set of data, for KBr, are shown in Fig. 4. It can be seen that ω_0 is the same for the two films, within the experimental error. It was found that the uncertainty in ω_0 determined from this data was about 5%. The uncertainty in ω_0 was about 10% for the samples of RbI, and about 3% for KCl. Values of ω_0, and $\eta(1-R)$ are given in Table I for the photon

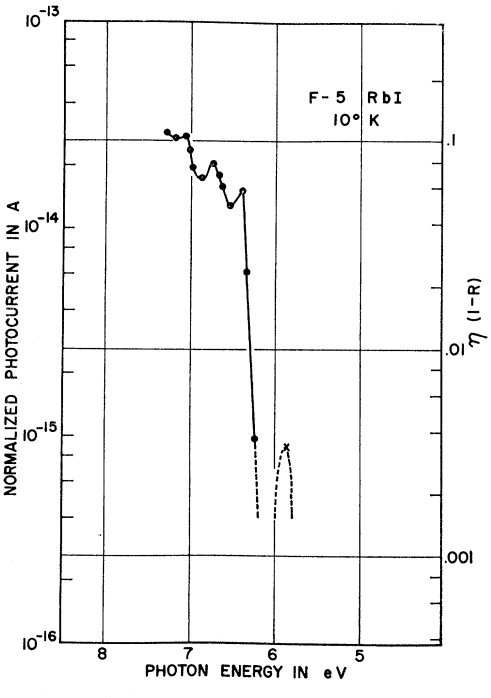

FIG. 6. Spectral response of RbI at 10°K.

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[10] K. Hecht, Z. Physik **77**, 235 (1932).

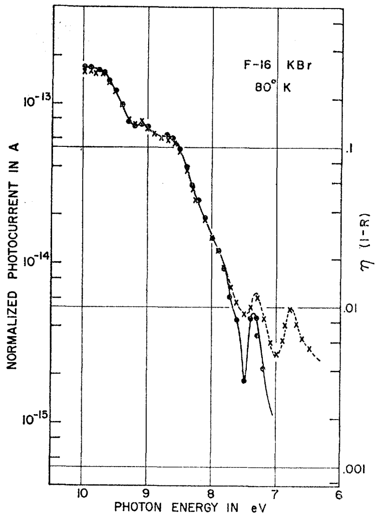

FIG. 7. Spectral response of KBr at 80°K.

energies shown. The measurements of ω_0 shown here were all made at 80°K.

B. Spectral Response of the Photoconductivity

Measurements were made of $\eta(1-R)$ as a function of photon energy, for films of RbI, KBr, and KCl at 80 and 10°K. These are shown in Figs. 5–10. These data were obtained with applied fields sufficiently large to saturate the photocurrent in each case. An absolute determination of $\eta(1-R)$ was made at only one photon energy. Values at other photon energies could be obtained from the measured values of photocurrent because it had been previously determined that the currents were directly proportional to the light intensity.

1. *Rubidium Iodide*

The spectral response of RbI at 80°K is given in Fig. 5. These results are for a RbI film evaporated on a fused silica substrate. The main feature is the sharp rise in the photocurrent of about 2 orders of magnitude starting at about 6.0 eV in the region between the two components of the spin-orbit doublet. This sharp increase is in the neighborhood of the step in the optical-absorption spectrum.

An inflection point appears on the rising photocurrent at about 6.25 eV which is near the second of the two absorption peaks observed on the "step" in the optical-absorption spectrum. Minima at 6.5 and 6.9 eV occur near the second component of the spin-orbit doublet and the absorption band which appears at 6.9 eV in the optical absorption.[5]

Because of the wide band pass of the monochromator, the two peaks in the optical-absorption spectra near the second component of the spin-orbit doublet cannot be resolved and consequently show up as only one minimum. There also appears to be a photoconductivity peak at 5.8 eV on the high-energy side of the first fundamental absorption line. This peak is difficult to detect because of the low signal level. The peak is dependent upon the length of previous ultraviolet irradiation and increases with prolonged exposure. It appears to be related to the presence of color centers produced by the ultraviolet light. The fact that it appears on the high-energy side of the first absorption peak is not understood. One would commonly expect a peak with such behavior to fall in the long-wavelength tail or the first fundamental peak and to be associated with the β band or bands due to other defect centers.

The spectral response of the photoconductivity at 10°K is given in Fig. 6. The current has the same general features as the photocurrent at 80°K but with a shift toward higher energies. It will be noted that there is also a general sharpening of the structure. The onset of strong photoconductivity is steeper and is well defined starting at about 6.15 eV where the current is down about two orders of magnitude from its maximum value. The low-energy peak now at 5.85 eV is still difficult to detect but remains on the high-energy side of the first fundamental absorption peak.

2. *Potassium Bromide*

The spectral dependence of the photoconductivity in a film of KBr at 80°K is shown in Fig. 7. This film was deposited in a LiF substrate. In KBr both components of the spin-orbit doublet are at lower energies than the "step" in the optical-absorption spectrum.[5] The response curve shows peaks which are dependent on the history of the irradiation and are located at the positions of each component of the spin-orbit doublet. A dashed curve indicates the growth of the peaks after the sample was irradiated with ultraviolet light for a period of time following the first run.

The photocurrent shows a pronounced increase at 7.5 eV in the region of the "step." A threshold for

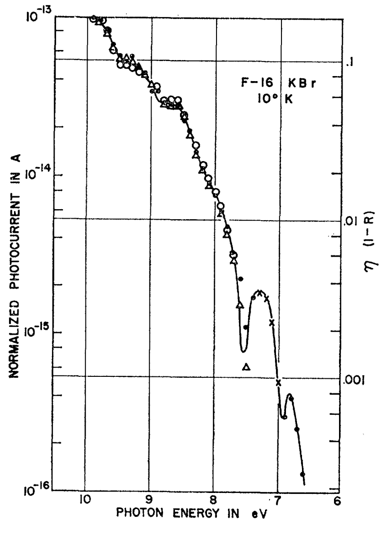

FIG. 8. Spectral response of KBr at 10°K.

photoconductivity is not as distinct as in the case of RbI, but on the other hand, the "step" and other features of the optical absorption also are not as distinct as RbI. The dip near 8.8 eV is apparently an effect due to the rapidly varying reflectivity.

The spectral dependence of the photoconductivity in KBr at 10°K is shown in Fig. 8. The dependence is essentially the same as at 80°K with a slight shift toward higher energies. The rise in the photocurrent is more pronounced than at liquid-nitrogen temperature. This effect is probably assisted by the fact that the sample has no previous irradiation since the runs at helium temperature were conducted first. As a result, the low-energy peaks are much lower and do not mask the other features.

3. Potassium Chloride

Photoconductivity as a function of photon energy for KCl at 80°K is given in Fig. 9. These measurements were made on a thin film evaporated on a LiF substrate. The features of the KCl photocurrent are similar to those of KBr, but with a general shift to higher energy, as would be expected. The photoconductive current rises rapidly beginning at a photon energy of about 8.2 eV where the current is down relative to its maximum value by over an order of magnitude. Figure 10 shows the photocurrent at 10°K. There are only small differences in the curves at the two temperatures. The structure at liquid-helium temperature is somewhat more pronounced, but the general features remain unchanged.

A peak occurs in the region of the spin-orbit doublet with some indication of a dip on the low-energy side. With 10-Å resolution this dip becomes evident and two peaks emerge. Neither of these peaks occurs at photon energies corresponding to the spin-orbit doublet. This is illustrated in the insert in Fig. 9. These peaks, as has been the case previously, are dependent on the duration of prior ultraviolet radiation in the fundamental region. The dashed line indicates this variation.

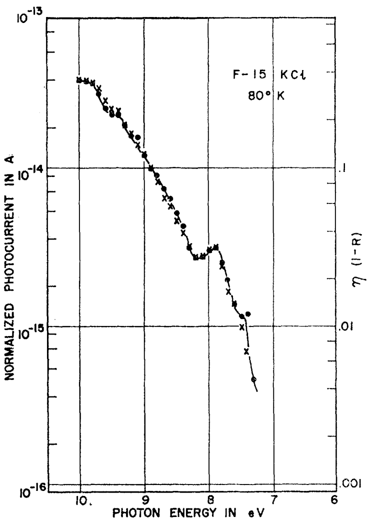

FIG. 9. Spectral response of KCl at 80°K.

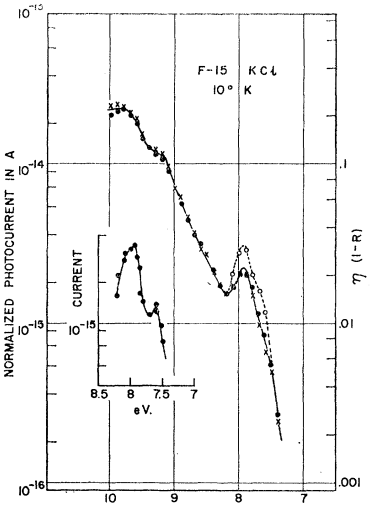

FIG. 10. Spectral response of KCl at 10°K.

CONCLUSIONS

A comparison between the photoconductivity data described above and the optical-absorption spectra of the three materials RbI, KBr, and KCl leads to some interesting conclusions.

A. Rubidium Iodide

At 80°K, the quantity $\eta(1-R)$ is less than 0.005 in the region of the first fundamental-absorption band. This is down by nearly two orders of magnitude from its value at 7.0 eV which is about 0.22. Nakai and Teegarden,[3] and Kuwabara and Aoyagi[4] also observed this decrease in the photocurrent in the first absorption band. The former authors found that the currents were smaller by at least a factor of 30 at photon energies corresponding to the peak of the first fundamental absorption relative to the maximum photocurrent in RbI.

The minimum occurring at about 6.5 eV near the second component of the spin-orbit doublet in RbI is a true minimum in the photocurrent. This can be seen by considering reflectivity data measured with higher resolution than that used in this work. The reflectivity on either side of the peak at 6.47 eV is about 10% and it rises to about 14% at its maximum.[11] This change in the reflectivity is insufficient to account for the minimum which occurs. This result suggests that competition is taking place between nonphotoconducting transitions and interband transitions when the sample is irradiated with photon energies corresponding to the second component of the spin-orbit doublet. This, as well as the result that the yield in the peak of the first

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[11] E. A. Taft and H. R. Philipp, J. Phys. Chem. Solids 3, 1 (1957).

fundamental-absorption band is down by nearly 2 orders of magnitude from its maximum value, supports the idea that bound states are formed at these energies.

A comparison of the spectral response of RbI at 80°K to the optical absorption measured at this temperature (see Fig. 1) shows that the photocurrent in the small absorption band at 6.09 eV, which is the band on the leading edge of the "step," is down by over an order of magnitude from the value of the current near 7.0 eV. At 10°K this band has shifted to 6.12 eV (see Fig. 2) and the photocurrents have diminished to about 2 orders of magnitude relatively to their maximum value. This suggests that the absorption band at 6.09 eV may also be a result of the formation of a nonconducting state.

The inflection point or shoulder, observed at liquid nitrogen temperature in the photoconductivity curve, occurs at the position of the second small absorption peak on the "step," at 6.23 eV (see Fig. 1). At this photon energy $\eta(1-R)$ has a value of 0.05 and the photocurrent is down by a factor of about 3 relative to its maximum value. At 10°K, no such structure is observed in the photocurrent. The position of the absorption peak has shifted to 6.26 eV and at this photon energy the photocurrent has dropped to over an order of magnitude below that of its maximum value near 7.2 eV. The value of $\eta(1-R)$ has decreased to about 0.005, an order of magnitude lower than at 80°K when stimulated at the corresponding photon energy of 6.23 eV.

These results may be explained in the following manner. The first three absorption bands in the optical-absorption spectrum, the first fundamental band, and the two small peaks on the "step," may be due to the formation of a series of bound states. At 10°K these states give rise to small photocurrents because of a small probability for thermal ionization. At 80°K, however, the probability for thermal ionization is much larger, especially for the third state. The current stimulated by 6.23-eV photons is therefore increased. The same effect occurs, to a smaller degree, in the case of the transition at 6.09 eV. Presumably the thermal-activation energy for the second state is higher than that for the third state. Assuming that such a process is taking place and that these states are being thermally ionized at 80°K but not at 10°K, an upper and lower bound can be placed on the thermal-activation energy of this third excited state at 6.23 eV. If E_{act} is the activation energy, then $0.0067\text{ eV} < E_{\text{act}} < 0.0008\text{ eV}$.

Assuming that the first three peaks in the optical absorption spectrum correspond to Wannier-Mott exciton states[9] as suggested by Fischer and Hilsch,[8] we may calculate the ionization limit using the relationship $h\nu_n = E_0 - G/n^2$, where E_0 is the ionization energy, G is the binding energy of the exciton and $n=1, 2, 3, \cdots$. If one neglects the first peak because its radius is too small for this state to be properly considered as a Wannier exciton, the ionization limit is 6.36 eV when calculated from the positions of the remaining two peaks at 6.09 and 6.23 eV and at a sample temperature of 80°K. The value of the ionization limit at 10°K is 6.37 eV. Within experimental error the first prominent peak in the spectral response curves occurs at the energy of the ionization limit. The data thus indicate a value for the band gap in RbI of 6.36 eV at 80°K and 6.37 eV at 10°K.

An interesting comparison to make is that of $\eta(1-R)$ and the quantum efficiency of photoemission at 7.0 eV. At this photon energy $\eta(1-R)$ is about 0.23 and the quantum efficiency of emission according to Philipp and Taft[11] is less than 10^{-3}. This is further evidence that over the range of photon energies employed, only photoconductivity was being observed in the sample. The *Schubweg* per unit field for RbI at 80°K was found to be 2.69×10^{-8} cm^2/V at an excitation energy of 6.5 eV.

B. Potassium Bromide and Potassium Chloride

The interpretation of the results of KBr and KCl is complicated by the fact that the optical-absorption data are not as complete as they are in the case of RbI. Without detailed absorption data in the region of the "step," it is difficult to make many comparisons or correlations between the optical-absorption spectra and the photoconductivity. We suspect, however, that the shoulder which appears in the spectra of both of these alkali halides is of the same nature as the shoulder in RbI. This would imply that the optical gap is about 8.0 eV in KBr and 8.9 eV in KCl, rather than 7.8 and 8.5 eV as previously suggested.[7]

In the case of KBr the *Schubweg* per unit field was found to be 1.31×10^{-8} cm^2/V at 80°K and an excitation energy of 8.6 eV. This is of the same order of magnitude as ω_0 for RbI. The *Schubweg* per unit field in KCl was found to be about an order of magnitude larger; that is, 2.00×10^{-7} cm^2/V at 80°K and an excitation energy of 8.6 eV. These values can be compared to the values of the same quantity obtained by Pohl and co-workers[12] for the case of KCl containing F centers. They found that at 173°K, was about 2×10^{-8} cm^2/V with 10^{16} (F centers)/cm^3, and was proportional to the numbers of F centers.

ACKNOWLEDGMENTS

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[12] R. W. Pohl, Proc. Phys. Soc. (London) **49** (extra part), 16 (1937).