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Intrinsic Photoconductivity
in the Alkali Halides

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INTRINSIC PHOTOCONDUCTIVITY
IN THE
ALKALI HALIDES

by

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Submitted in Partial Fulfillment
of the
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DOCTOR OF PHILOSOPHY

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VITA

George Rodney Huggett was born in Fargo, North Dakota on August 26, 1936. He entered the University of Illinois in September, 1954 and the following year transferred to Oklahoma State University. In 1958 he received from this university the Bachelor of Science degree with a major in physics.

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He enrolled in the graduate school of the University of Rochester in the Institute of Optics in September, 1961. Since then, to the present, he has held teaching and research assistantships. The research assistantship was under the supervision of Dr. K. Teegarden, on problems primarily concerned with photoconductivity in the alkali halides.

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ABSTRACT

Photoconductivity in thin films of RbI, KBr, KCl and RbCl has been measured at temperatures of 10°K and 80°K. Photocurrents were stimulated by irradiating the sample in the fundamental absorption region with ultra-violet light. Saturation curves showing the dependence of photocurrent on the applied voltage were also obtained. The schubweg of the electrons and the absolute value of the quantum efficiency times one minus the reflectivity $[\eta_a(1-R)]$ were determined. The experimental data are compared to the optical absorption spectra. In the region of the first fundamental absorption $\eta_a(1-R)$ was down by about two orders of magnitude from its maximum value. The absorption peaks in the region of the "step" were assumed to fit the Wannier model as suggested by Fischer⁸ and Baldini.⁹ In RbI the value of $\eta_a(1-R)$ at the photon energy corresponding to the peak at $n = 2$ was down from its maximum value by over an order of magnitude at 80°K and by about two orders of magnitude at 10°K. Its value in the peak corresponding to $n = 3$ was only down by about a factor of three at 80°K and by over an order of magnitude at 10°K. The band gap at 80°K for the materials estimated

from these curves are: RbI, 6.36 ev; KBr, 8.0 ev; KCl, 8.9 ev, and RbCl, 8.5 ev.

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CHAPTER I

INTRODUCTION

A. Electronic States of Ideal Insulators

The study of the properties of solids by theoretical and experimental investigators was begun in the early 1900's. The qualitative existence of bands was first pointed out by Strutt¹ in 1927. This band concept which was extended by Brillouin,² Peierls,³ and others, characterized ideal insulators with a filled valence band and an empty conduction band. Since the electrons in a filled band can make no contribution to the electric current, a current in an insulator, in particular the alkali halides, is only possible if electrons are placed into the empty band, either from outside or by transitions from lower bands.

1. Inter-band Transitions

Inter-band transitions may occur between these bands if the total wave vector is conserved. The photon wave vector is negligibly small, hence for direct optical transitions it is sufficient to assume $k = k'$, where k and k' are the initial and final wave vectors. An electron in a given state k in the valence band may make an

optical transition only to a state with the same value of k in the conduction band and the energy of the absorbed photon is related to k by

$$h\nu = E_c(k) - E_v(k),$$

where c and v refer to the conduction and valence bands.

As the photon energy is decreased, there will be an energy below which band-to-band transitions can not occur. This energy corresponds to the width of the forbidden energy region or band gap.

Other inter-band transitions may occur as a result of X-ray absorption by the inner electrons. These transitions are important in studying the electronic structure, but they are not pertinent to this work.

2. Exciton States

Band theory is known to generally provide a good basic description of electronic structure of solids. The description of ideal insulators by this theory establishes a forbidden energy region within which there can be no electronic states. The idea that electronic states of pure crystals do, in fact, exist within this so-called "forbidden" region, was first introduced by Frenkel⁴ and this concept of excitons was further developed by

Peierls.⁵

The Heither-London model used to describe the excited state of a perfect crystal, predicts a series of states leading to a series limit in addition to the continuous band predicted by band theory. These excitons can be considered in two limiting approximations which are distinguished by the strength of the bond. In the one due to Frenkel,⁴ the exciton is considered tightly bound and the excitation remains localized within the unit cell. In the other approximation due to Mott⁶ and Wannier,⁷ the exciton is weakly bound and the excitation is spread over many cells. In any case, excitons carry no net charge and although they may be mobile, can not give rise to an electric current.

Excitons in the alkali halides have generally been considered to be of the Frenkel type. In other materials such as CuO and CdS Wannier excitons have been observed. Recent measurements of the optical absorption spectra of the alkali halides by Fischer and Hilsch⁸ show a peak in absorption on the high energy side of the first fundamental band in KI and RbI which they interpreted as being the second exciton state in a Wannier exciton series. Recently Baldini⁹ has observed an additional peak in this

region which may correspond to the third excited state of the series. Until an additional peak is observed, since the radius of the first excited state is too small to be considered a Wannier exciton, we can only say that they appear to fit into the Wannier exciton scheme. It may be that the more correct model for the exciton in the alkali halides is intermediate between the limiting cases of Frenkel and Wannier.

3. Summary

The band theory of solids leads to the prediction that insulators, such as the alkali halides, will be transparent in the spectral region between the Restrahl absorption in the infrared and an absorption edge in the visible or ultraviolet corresponding to the onset of band-to-band transitions. The possibility of non-conducting excited states of the crystal, such as excitons, complicates the picture somewhat and makes an analysis of the electronic states of an insulator from simple optical absorption measurements impossible. For example, one can not generally determine the band gap of an insulator by optical absorption measurements alone.

If the electronic states of an alkali halide

crystal could really be classified into those which lead to photoconductivity and those which do not, photoconductivity measurements could be used in conjunction with absorption measurements to differentiate between excitons and inter-band transitions. Unfortunately, exciton transitions can give rise to photoconductivity by several secondary processes, which will be discussed later. Thus photoelectric measurements may be only partly successful in detecting band-to-band transitions. In addition to this, photoelectric measurements in alkali halides are difficult. Measurements of photoconductivity are necessary, however, before many more sophisticated experiments can be attempted.

B. Optical Absorption Spectra

The earliest work on the optical absorption of many of the alkali halides was carefully done by Hilsch and Pohl.^{10,11} They were the first to use thin evaporated films of materials with high absorption constants. Additional optical absorption measurements were made as a function of wavelength and temperature by Schneider and O'Bryan¹² and others.¹³⁻¹⁷

More recently Eby, Teegarden, and Dutton¹⁸ have

measured the absorption spectra of evaporated films of the alkali halides, with the exception of LiF, at room temperature and have also extended the measurements to liquid nitrogen temperature. Figure 1 shows the absorption spectra of KCl, KBr, and RbI.

As the temperature is lowered, the structure becomes more pronounced. The strong absorption bands narrow and shift toward higher energies. The long wavelength tail of the first band has been found to exhibit a simple exponential dependence of absorption constant temperature and photon energies over five orders of magnitude of the absorption constant.¹⁷

The strong absorption band on the long wavelength side of the region of electronic absorption has been associated with the formation of excitons. This interpretation of the nature of the absorption band was made apparently because no photoconductivity could be observed during irradiation in the band. Since no satisfactory observation of photoconductivity at any wavelength in the alkali halides was available, this identification of exciton transitions seems to have been premature. Other evidence for the existence of excitons in the alkali halides was presented by Apker and Taft and will be

FIGURE 1. ABSORPTION SPECTRA OF KCl, KBr AND RbI FROM Eby et al. (18)

discussed later.

The two lowest energy absorption bands in the alkali halides have an energy separation that is characteristic of the spin-orbit interaction in the ground state of the halogen ion. In the crystals, this halogen doublet has an energy separation of 0.12 ev for the chlorides, 0.50 ev for the bromides, and 0.90 ev for the iodides at liquid nitrogen temperature.

A shoulder in the optical absorption spectra of most of the alkali halides is observed on the high energy side of the first two bands. In the iodides, except CsI, this shoulder occurs between the bands, for example, at 6.1 ev in RbI at liquid nitrogen temperature. This shoulder or step becomes pronounced at liquid nitrogen temperature, and shifts toward higher energies. Philipp and Taft¹⁹ have observed a threshold for photoemission in a number of alkali halides on the high energy side of this step. As a result of these measurements, they assumed this step or edge indicated the onset of band-to-band transitions, since this assumption was consistent with the onset of photoemission. The work of Fischer and Hilsch,⁸ as discussed above, shows that the structure of the step is not as simple as previously thought. The

measurements by Baldini⁹ show two peaks on the shoulder, indicating that the step is probably composed of a series of absorption bands and can be interpreted as the exciton series.

Recent measurements of optical absorption spectra by Baldini²⁰ of solid inert gases which exhibit several similarities to the alkali halides in electronic configuration, show this same step in unannealed film. When the films are annealed the step can be resolved into a similar series of peaks which he has interpreted as being due to the formation of Wannier type excitons. These peaks tend to obscure any underlying structure that might be associated with the inter-band transition density of state, hence making a determination of the band gap from optical absorption data difficult. Although approximate values of the band gap have been obtained, other measurements must be made to yield more accurate values.

C. Photoemission Measurements in Alkali Halides

A great deal of the recent photoelectric investigations of alkali halides have been done by Apker, Philipp, and Taft.²¹⁻²⁷ They have measured the dependence of the photoelectric yield on photon energy and the

energy of the photoelectrons emitted at any given photon energy by retarding-potential techniques. To measure the frequency dependence of the photoelectric yield, the configuration usually used was an emitter surface enclosed in a metal collecting cylinder with a hole to admit the radiation. For energy distribution measurements more intricate arrangements were used, but basically they consisted of a small emitter within a large spherical collector to obtain approximate spherical symmetry and the retarding potential applied between the electrodes.

Photoelectric yield curves of the iodides obtained by Taft and Philipp¹⁹ are shown in Figure 2a. They observed no photoemission from the pure samples in the visible or near ultraviolet, which included the region of the first exciton peak and the shoulder in the optical absorption spectra. In most materials, a threshold for photoemission occurred about 1 ev above the position of the shoulder. The curve rises rapidly, showing no structure at higher photon energies and reaches efficiencies greater than 10 per cent. However if F-centers are present, Apker, Philipp and Taft²¹⁻²³ have observed photoemission from thin films and single crystals in the visible as well as throughout the fundamental absorption

FIGURE 2a. PHOTOEMISSION OF PURE IODIDES FROM TAFT AND PHILIPP (19)

FIGURE 2b. PHOTOEMISSION OF KI CONTAINING F-CENTERS FROM TAFT AND PHILIPP (23)

region. The spectral distribution of the yield for a single crystal of KI studied by Philipp and Taft²³ is shown in Figure 2b. The features are similar to the emission from thin films. For incident photon energies below 5 ev the emission is attributed to the direct ionization of F-centers. At 80°K photoemission begins to appear at incident quantum energies of about 1.6 ev. This emission has been interpreted as resulting from the direct photoionization of F' centers.²⁴ At 5.5 ev a peak can be resolved which is associated with the β -band and exciton-induced emission from F-centers.²⁵ The emission continues to increase with increasing photon energy, peaking with the first fundamental absorption peak at 5.8 ev. The interpretation given for the emission from the fundamental absorption has been that excitons are formed which ionize the F-center in a secondary process. The peak at 5.5 ev is also exciton-induced emission, but in this case the exciton is initially trapped at its point of decay.

The energy distribution of photoelectrons from RbI studied by Apker and Taft,²⁶ was found to have two peaks. The high energy peak shifted to higher energies with increased photon energy and the low energy peak remained

stationary. The high energy peak has been associated with electrons directly photoionized from F-centers and the low energy peak associated with exciton-induced photoemission.

Exciton series structure in the photoelectric emission from RbI containing F-centers has been observed by Taft and Philipp.²⁷ A second emission peak seen at 20°K which coincides with the second peak in the first exciton series.^{8,9} This peak is also interpreted as being due to exciton-induced emission from F-centers.

These experiments demonstrate that energy is indeed transferred from excitons produced by optical absorption in the fundamental region to F-centers, both in the ionization and production of the centers. This does not necessarily imply the migration of excitons, since in these experiments the F-center concentrations were sufficiently high that other mechanisms, such as dipole-dipole interaction, could be responsible for the energy transfer over these distances.²⁸ Also, experiments by Teegarden and Weeks²⁹ have shown that free charge carriers are important in producing luminescence in undoped KI crystals irradiated in the region of the first fundamental band.

This result suggests another mechanism for the transfer of energy between the electronic transition associated with the first fundamental band and an F-center. Recombination of an electron and a hole near an F-center might result in its destruction.

Taylor and Hartman³⁰ have studied the photoemission from thin films and single crystals of NaCl and KCl, using the method of Apker et al. Photoelectric yield and the distribution of energy of emitted electrons were measured using a geometry similar to that discussed previously. They observed smooth photoelectric yield curves with a threshold at about 8.1 ev for NaCl and 8.4 ev for KCl. They concluded from their measurements that the valence band is about 8.3 ev below the vacuum level for both materials and that the 1.5 ev difference between the high-energy foot of the reflectivity peak and the onset of emission might be interpreted as the possible width of the valence band of KCl.

D. Photoconductivity Measurements in Alkali Halides

Electron motion in highly insulating crystals resulting from irradiation with light was definitely established in diamond, by Gudden and Pohl³¹ in 1920. Many other materials were soon found that exhibited

similar properties when irradiated near the fundamental absorption edge. The early studies of photoconductivity in the alkali halides by Pohl³² and his co-workers were done in colored crystals in which the F-center provided the source of electrons. They interpreted the primary photocurrent in terms of a mean range (schubweg) for electronic motion in the direction applied field. After exhaustive measurements they determined that the schubweg was proportional to the electric field strength and governed by a uniform volume distribution of traps. The range per unit field was found to be inversely proportional to the F-center concentration, implying that the F-center is the primary trap in the case of colored crystals. More recently, Inchauspe³³ has measured photoconductivity in colored crystals irradiated near the tail of the first fundamental band in the vicinity of the β -band. These currents were interpreted as exciton-induced photoconductivity.

In a very high electric field an electron released by light in a thin crystal may be collected at the anode. In this case, the schubweg becomes comparable to the crystal dimensions and the primary photoelectric current then becomes saturated. Flechsig³⁴ demonstrated that

such an effect can be observed in the thin colored alkali halide crystals. Hecht³⁵ related the current-voltage curve, for a saturated sample, to the schubweg and crystal thickness, in the case of uniform absorption, thus providing a means of determining the schubweg from a saturation curve. Witt³⁶ measured a range per unit field of $2.3 \times 10^{-8} \text{ cm}^2/\text{volt}$ in NaCl containing 1.3×10^{15} F-centers per cc with conductivity induced by α -particles. Harten³⁷ using X-rays to irradiate colored KCl, gives a value of 10^{-8} to $10^{-9} \text{ cm}^2/\text{volt}$ for the unit range.

Several attempts have been made to observe intrinsic photoconductivity in alkali halide crystals. Before the war, Ferguson³⁸ made photoelectric measurements on sodium chloride in an attempt to test the exciton theory by comparing the wavelength dependence of photoconductivity and absorption for an alkali halide. His experimental arrangement consisted of two electrodes mounted behind his crystal and the crystal placed between them and the exit slit of a windowless vacuum monochromator, using a capillary air discharge tube for a light source. The electrodes were placed behind the crystal to try to measure a volume conductivity. Around the sample and holder was a cylindrical brass shield which was used to

make external photoemission measurements. The current measurements were made as follows: A high potential was applied across the sample electrodes and the current due to photoemission and photoconductivity measured, then applying a small reverse voltage on the crystal electrodes and a large accelerating voltage on the brass shield, the photoemission was measured. He measured no currents if the crystal was removed. By subtracting the value of the second measured current from the first, he arrives at a value for his photoconductive current. He points out that in the region between 1300 and 1350 Å in which there is large absorption the absence of a measurable photocurrent indicates the existence of exciton states and that his data show structure in both photoemission and photoconductivity between 9.4 and 10.2 ev.

Other investigators³⁰ at the same laboratory have later attributed these currents not to photoconductivity but to copious photoelectric emission from metallic electrodes illuminated by reflected light from the crystal. It should be pointed out that the region of known exciton absorption is between 1500 and 1600 Å, a region not considered in the preceding results. These photoemission data also are not compatible with that taken by Taylor

and Hartman,³⁰ nor with other photoemission data taken on other alkali halides which show a smooth curve over the corresponding region.

Taylor and Hartman made an extensive search for internal photoconductivity in NaCl, KCl, KI and LiF with photon energies ranging from 6 ev to 21 ev. Many schemes and electrode arrangements were tried, all with negative results. Their crystals were irradiated with a hydrogen discharge lamp whose light was passed through a grating vacuum monochromator. The sample was mounted behind the exit slit with no window to separate the detector head from the monochromator chamber. Current measurements were made with a vibrating reed electrometer which had an input resistor of 10^{12} ohms. The basic arrangement used consisted of a crystal which was irradiated longitudinally with the applied field. An electrode backing the crystal was connected to the electrometer, and a cylindrical collector electrode used for emission measurements served to charge the crystal and collect emitted electrons. In some cases a front transparent electrode was employed to establish the electric field. One method relied on the electrostatic potential between the external collector and the back electrode to polarize the crystal

and establish an electric field. A second method consisted of charging the surface by emission from a piece of tantalum which was irradiated by a mercury source. Another used a transparent front electrode of fine nickel screen or evaporated gold to maintain the potential across the crystal. All attempts to measure photoconductivity were negative.

Similar methods were tried on extremely thin samples which were water-etched and then annealed at 500°C for an hour. After annealing, a thick gold electrode was evaporated on the back. Again the results of each variation were negative. Unsuccessful experiments were tried in which the samples were thin films evaporated between a thick gold substrate and a transparent gold surface electrode.

In an attempt to measure surface photoconductivity, they evaporated gold electrodes on the surface of single crystals leaving a 2-mm separation between them. LiF was then evaporated over the entire surface to suppress emission. A voltage of 1500 volts was applied between the electrodes. Again, no positive results were obtained except for emission from the LiF.

These measurements were all conducted at room

temperature where polarization of the sample can arise due to ionic conductivity. This polarization can occur with the voltage on, even in the dark. Due to ionic conductivity and polarization, it is usually convenient to perform these measurements at lower temperatures. Also a clean vacuum system is desired, since it is known that contaminants such as diffusion pump oil exhibit luminescence and photoemission when irradiated with ultraviolet light.

In an experiment attempting to measure the internal photoelectric effect, one must be able to rule out external photoemission completely. If emission occurs, the contribution to the measured signal due to photoconductivity is usually completely obscured. This is due to the fact that the mean free path of photoemitted electrons is much larger than the length of their trajectory from the point of emission to the anode. Hence, for every photoemitted electron the charge measured by the external circuit is nearly one electronic charge. On the other hand, the mean range of a photoconductive electron is extremely short. In a typical case with an electrode separation of 10^{-1} cm and the applied field as high as 10^4 volts/cm, the mean range of the electron is 10^{-4} cm

and the measured charge is $10^{-5}e$. Consequently, there must be 10^5 photoconductive electrons for every photoemitted electron just to obtain the same order of magnitude for their contributions to the total photocurrent. For this reason one must suppress photoemission completely or use such a configuration that photoemission can not occur, before any measurement of photocurrent can be considered reliable.

In 1959, Teegarden³⁹ conducted preliminary investigations of the internal photoelectric effect in KI and RbI. To measure photoconductivity he evaporated aluminum electrodes with a 1-mm separation on the surface of the crystals. A third electrode made of wire mesh was placed several millimeters in front of the sample. This electrode, a collector, was used to measure and check photoemission.

He used two effective methods to suppress photoemission from the crystals. The surface was coated with a thin film of KCl, about $1000 \text{ \AA}$ thick, or measurements were made in an inert atmosphere of nitrogen gas which tended to quench the photoemission. It was found that photoemission disappeared completely upon coating with KCl. With the dry nitrogen atmosphere, photoemission was

suppressed except for photon energies near 6.5 ev.

Prior to coating his samples, the photoemission measurements of RbI were very similar to those of Apker, Philipp and Taft. Measurements using the photoconductivity electrodes showed the same general behavior. After evaporation of the KCl the photocurrent showed pronounced threshold around 6.0 ev and the magnitude of the currents in this region did not depend upon previous exposure to ultraviolet radiation as do photoeffects from F-centers.

More recently, Nakai and Teegarden⁴⁰ continued this investigation with another configuration and a considerably cleaner vacuum. The crystal was placed between two parallel plate electrodes with thin mylar sheets on both sides of the crystal to provide blocking electrodes. KCl was evaporated over the surface to prevent photoemission. The source was a low-pressure hydrogen discharge tube whose light was passed through a quartz prism monochromator and then focussed on the crystal with a quartz lens. A clean vacuum was maintained by using a molecular sieve fore pump and a gettering high-vacuum pump.

The photocurrent measured for RbI and KI indicated a band gap of about 6.0 ev. They observed a threshold that seems to correspond to the step in the optical absorption spectrum which had been previously interpreted as the onset of inter-band transitions. In the region of the second exciton peak, the photocurrent went through a minimum in which the magnitude decreased by a factor of two or three. Small photocurrents were measured on the low energy tail of the first fundamental absorption band which increased with prolonged irradiation with ultra-violet light. The current was linearly related to the intensity when stimulated with 6.2 ev photons, but appeared to rise as the square of the intensity when stimulated with photons of 5.6 ev and lower energies, hence implying a secondary process. It is believed that these currents are due to the photoproduction and destruction of color centers in the crystal.

CHAPTER II

BASIC THEORY

Photoconductivity is measured with a configuration shown in Figure 3 which is basically quite simple. The sample is mounted between two electrodes and a voltage is applied. Upon illumination, either throughout the sample or in only a small slice, a current passes through the circuit and is measured by the electrometer. The observation of primary, as distinguished from secondary, photocurrents is subject to several restrictions.⁴¹⁻⁴³

The primary current is the direct photoelectric current which is of interest. Space charge limitations, entrance of charge at the electrodes, and charge multiplication must not occur. These are usually prevented by the use of blocking electrodes, low light intensities, and photon energies insufficient to produce charge multiplication.

Consider an insulating crystal placed between two blocking metallic electrodes with a potential difference V applied across them. The energy diagram for such a system is shown in Figure 4. The valence band of the crystal is completely filled and the conduction band completely empty. Suppose a slice of the sample is

FIGURE 3. BASIC CIRCUIT FOR MEASURING PHOTOCONDUCTIVITY.

FIGURE 4. ENERGY DIAGRAM FOR INSULATING CRYSTALS.

illuminated with light of photon energies in excess of the band gap, where $E_g = E_c - E_v$, electron-hole pairs will be produced resulting in free electrons in the conduction band and holes in the valence band. The holes are extremely immobile in the alkali halides at least, hence only the electrons need be considered in discussing charge motion. The electrons released by the light are now free to move in the crystal and will drift under the influence of the applied electric field. All of the electrons do not reach the anode, however; the electrons drift a certain distance and are then trapped at trap sites, indicated in Figure 4 by E_{T1} , or by direct recombination with holes. The current due to the motion of these electrons is essentially proportional to the applied voltage for weak fields. In zero field the electrons execute a kind of Brownian motion while they are free to move. When a field is applied to the crystal, the electrons will still tend to undergo their Brownian path but they will have a drift due to the applied field superimposed on the random motion. The net result will be that the electrons will be trapped in positions, on the average, nearer the anode than in the zero-field case. In

the zero-field case, just as many electrons will migrate toward the cathode as toward the anode and consequently there is no net charge induced upon the electrodes. However, with an applied field there is a net drift and the charge induced on the electrodes is measured by the electrometer. This same charge could have been measured if every electron had drifted a distance w due to the field. This distance w is called the mean range or schubweg, of the photoelectrons.

In the present experiment the sample of thickness ℓ was placed between two electrodes and illuminated through a small slit in the cathode by strongly absorbed ultraviolet light. The field was derived from a voltage V that was applied across the electrodes and the electrometer was connected in series with the battery and crystal. The electrons excited into the conduction band migrate toward the anode until they are trapped. We assume that, if an electron is free, the probability per time dt that it will be trapped is dt/τ . Then the number of electrons remaining after a time t is given by $n_0 e^{-t/\tau}$ where n_0 is the initial number of electrons excited, and τ is the mean trapping time. Also $\tau =$

$1/N_t \sigma \mu$, where N_t is the concentration of uniform traps, σ is the trapping cross section and μ is the mean thermal velocity of the electron. The schubweg is given by $w = \mu E \tau$ where μ is the electron mobility and the range per unit field is $w_0 = \mu \tau$. Using $t = \frac{x}{\mu E}$ and $\tau = w/\mu E$ then $n = n_0 e^{-x/w}$ given the number of free electrons that have traveled a distance x into the crystal. If an electron between the electrodes travels a distance x , the charge induced on the electrodes and measured by the electrometer is $q = e x/l$. The net charge measured by the electrometer due to a given light pulse can be calculated if one considers that some of the electrons may be collected at the anode and the light has a finite penetration depth.

If I_0 is the intensity of the incident light, the intensity a distance x in the sample is $I = I_0 e^{-\alpha x}$ or in terms of the number of photons, which is of interest here, $N = N_0 e^{-\alpha x}$ where N_0 is the number of incident photons and α is the absorption coefficient. Actually, if the photons are incident on a sample having a reflectivity R , the number entering the sample is $N_0 (1 - R)$. The number of photons absorbed in the sample in an

interval between x and $x+dx$ is $dN = -\alpha N_0 (1-R) e^{-\alpha x}$.

Integrating from 0 to l yields the total number of electrons released in the sample, $n = \eta_a N_0 (1-R) (1 - e^{-\alpha l})$

where η_a is the quantum efficiency per absorbed photon.

The total charge measured by the electrometer is therefore

$$Q = ne \frac{\bar{x}}{l} \quad \text{or} \quad Q = e \eta_a N_0 (1-R) (1 - e^{-\alpha l}) \frac{\bar{x}}{l}$$

where $\bar{x}$ is the mean distance drifted by an electron.

The saturation factor is defined as $\psi = \bar{x}/l$ and takes into account the mean range of the electron and the finite depth of optical absorption. It can be derived by calculating the total displacement of all the electrons and dividing by n , the number of electrons excited. The total displacement is made up of two parts; first is the distance drifted by the electrons that are trapped in the sample volume and do not reach the anode, and second is the distance drifted by the electrons that do reach the anode and are collected. The expression for ψ in the case where the illuminated electrode is negation is

$$\psi = \frac{1}{1 - e^{-\alpha l}} \frac{\omega}{l} \left[1 - \frac{e^{-\alpha l}}{1 - \omega} + \frac{\alpha \omega}{1 - \alpha \omega} e^{-l/\omega} \right]$$

In the limit as $\alpha \rightarrow \infty$ which corresponds to all light being absorbed at $x=0$, $\psi = \omega/l (1 - e^{-l/\omega})$. This formula was derived by Hecht.³⁵ In the other limit as $\alpha \rightarrow 0$ corresponding to uniform absorption

$$\psi = \omega/l [1 - \omega/l (1 - e^{-l/\omega})] .$$

For complete saturation of the photocurrent, i.e., $\omega = \infty$, the quantity ψ approaches unity in the case $\alpha \rightarrow \infty$ and approaches one-half in the case $\alpha \rightarrow 0$.

Combining the expression for ψ with that for the measured charge, one sees how the saturation factor determines the charge flow in the external circuit for given values of l and ω . Measuring the charge as a function of the applied voltage, will produce a curve that will show saturation effects if a high enough voltage is applied. Since the range ω is proportional to the applied field E , fitting the theoretical saturation curve to the experimental data will determine ω . By making an additional measurement of the photon flux, N_0 , one can then calculate $\eta_a(1-R)$ from the expression

$$Q = e \eta_a N_0 (1-R) (1 - e^{-\alpha l}) \psi .$$

CHAPTER III

EXPERIMENTAL APPARATUS

A schematic diagram of the experimental arrangement used for the measurement of photoconductivity and to monitor the incident radiation is shown in Figure 5.

A. Monochromator

The vacuum monochromator used in this work was designed by Smith.⁴⁴ It was a smaller version of an instrument designed by Dr. K. J. Teegarden and used by Eby.¹⁸ Their instrument was similar in design to one that was constructed by Tousey.⁴⁵ A detailed description of the monochromator was given by Smith and also discussed by Knapp.⁴⁶

A Bausch and Lomb concave diffraction grating was mounted on an arm which was pivoted at the center of a 40-cm Rowland circle. Rotation of this arm translated the grating along the circle, thereby changing the wavelength of the light emerging from the exit slit of the monochromator. The grating was ruled at 600 grooves/mm with a ruled area of 38 mm by 30 mm. The radius of curvature of the grating was 400.7 mm. It had a tripartite blaze with a blaze wavelength of 1216 Å and a blaze angle of 2°5'.

FIGURE 5. DIAGRAM OF EXPERIMENTAL ARRANGEMENT

The entrance and exit slits were fixed on the Rowland circle such that the angles of incidence and reflection were 10 degrees for the zero-order spectrum. The slits were continuously adjustable in width from 10 microns to 1.5 mm and were 9 mm long. The linear dispersion at the exit slit was $41 \text{ \AA/mm}$ at a wavelength of approximately $1500 \text{ \AA}$. The f/speed of the monochromator was $f/10$ in the horizontal plane and $f/13$ in the vertical plane. Wavelength could be determined to an accuracy of $\pm 1 \text{ \AA}$ by a counter connected to the grating drive mechanism.

Scattered light was reduced by appropriately positioned baffles within the monochromator and within the shutter and mirror assembly. The contribution to the photoconductive signal due to scattered light was negligible. The only correction necessary was in the intensity measurement, in which the contribution due to the scattered light was subtracted.

B. Source

The ultraviolet radiation source was a Hanovia quartz discharge lamp, one end of which opened into the vacuum monochromator via the entrance slit. Hydrogen gas

used for the discharge was introduced into the lamp by a needle valve and leaked into the monochromator through the entrance slits. The hydrogen gas pressure was about 0.5 torr in the capillary. The lamp was operated at 1140 volts D. C. and drew 370 mA dissipating about 420 watts. Stable operating conditions were obtained after the lamp had been allowed to warm up for 30 to 45 minutes.

C. Pumping Systems

The monochromator and the shutter and mirror assembly were evacuated by a Consolidated Electrodynamics type MCF-60 water-cooled oil diffusion pump with a Welch model 1402B mechanical forepump. Back-streaming pump oil vapor was reduced by a right-angle water-cooled baffle which connected the diffusion pump to the monochromator vacuum chamber.

The pressure in the chamber was measured by calibrated General Electric type G-5 thermocouple gauge. In operation, with hydrogen entering the chamber from the lamp, the pressure was typically 10^{-2} torr.

Evacuation of the cryostat to a pressure of about 20 microns was accomplished with a Varian Vac Sorb Fore-pump Model 941-5610. The pumping action of a Vac Sorb

pump was achieved by the sorption of gas molecules by a chilled material called a molecular sieve. At a pressure of 20 microns an ion-gettering pump, a Varian 5-liter-per-second Vac Ion pump Model 911-1402, was started. The power supply for this pump was a Varian Model Va-1304 which also measured the pressure in the cryostat, since the current drawn by the pump was proportional to the pressure. After this pump had been started, the forepump was valved off and allowed to warm to room temperature. An advantage of these pumps was that an extremely clean system could be maintained; in particular all traces of oil which may come from a mechanical forepump and from a diffusion pump were eliminated. Also, the pumps contained no moving parts, hence there was no problem of vibration which could produce microphonics. The pressure obtained in the cryostat was typically 10^{-8} torr with nitrogen in the outer jacket of the cryostat. When helium was introduced into the helium reservoir, the pressure dropped to approximately 10^{-9} torr.

D. Shutter and Mirror Assemblies

The shutter consisted of an aluminum vane mounted on the armature of a Ledex rotary solenoid, size 1E with a

rotary stroke of 45 degrees. The rotary solenoid employed the inclined plane to convert linear motion to direct rotary motion. Power was supplied to the solenoid by a Ledex full wave rectifier type B-6162B which in turn was controlled by an Eagle Signal Corporation Microflex timer type HA12A6. The time interval could be varied from 1/10 to 120 seconds with an accuracy of about 1/10 of a second; the interval was typically 10 seconds for most measurements. The shutter could be opened at any time by a push-button that initiated the timer cycle.

The mirror assembly consisted of a movable front surface aluminized spherical mirror with a radius of curvature of 12 inches. It imaged the exit slit on the sample with a magnification of 1. The mirror could be manipulated from outside while the system was evacuated to permit positioning of this image on the sample. The aluminum coating was done by Evaporated Metals Co., Ithaca, New York.

Both the shutter and mirror assemblies were contained within a housing which was evacuated through the monochromator. This housing served as an evacuated path for the ultraviolet radiation between the exit slit of the monochromator and the cryostat, which contained the

sample. The housing also contained a sodium salicylate phosphor which could be moved in and out of the beam as desired. A photomultiplier was mounted so that a portion of the luminescence from the phosphor was incident on it through a window in the side of the housing.

As mentioned earlier, the major difficulty in making photoconductive measurements was differentiating between the photoemissive and the photoconductive contributions to the measured photocurrent. For every photoemitted electron there must be about 10^5 photoconductive electrons just to produce a photoconductive signal of the same order of magnitude as the photoemissive signal. From this simple consideration one can easily see that if emission occurs, the contribution to the measured signal due to photoconductivity would be completely obscured. For this reason photoemission was suppressed or a configuration was used in which photoemission could not take place.

Control of external photoemission was the prime reason for the particular design of the mirror and shutter housing. Another design was considered in which the slit in the sample holder was to be the exit slit of the monochromator. This would provide maximum intensity and

the illumination of the sample would be independent of the changing angle of emergence. This design would be quite useful for cases in which one wished the illuminated region of the sample to be precisely located. This design was rejected since the ultraviolet radiation at other wavelengths than the wavelength focused at the slit would be spilled throughout the cryostat. The result would be photoemission from all the metal parts illuminated and consequent large background photocurrents would mask any internal photocurrent most efficiently.

The mirror and shutter housing used had the disadvantage of adding a reflecting surface and consequently reducing the intensity. On the other hand this design separated the sample from the exit slit with a separation of 24 inches. This distance which the electrons emitted at the exit slit must traverse was field free except for that due to the space charge of the electrons themselves, hence discriminating against electron drift toward the sample. A fused silica or a LiF window separated the cryostat from the mirror and shutter housing, hence isolating one from the other. The isolation was primarily to separate the two pumping systems, but also served to impede any electron drift. The added optical path also

provided for the addition of baffles to improve upon the reduction of scattered light. It was felt that this design was one of the features that made this experiment successful. The proximity of the sample to the exit slit in the apparatus of other investigators may be an explanation for their rather ambiguous results.

E. Samples

The alkali halides used, with the exception of KCl, were grown by Dr. Karl Korth of Keil, Germany, by the Kyropoulos method. The KCl was obtained from Harshaw Chemical Company. The samples were in the form of thin films evaporated on lithium fluoride or fused silica substrates which were 1 inch in diameter and approximately 1 mm thick. A schematic diagram of the samples is shown in Figure 6. The alkali halide A was evaporated in a circular area with a diameter of $1/2$ inch in the center of the substrate S. An aluminum film F was then evaporated, also with a circular area but with a diameter of $5/8$ inch, over the sample. In this manner, a sandwiched sample configuration was formed. The evaporations were performed successively in the same vacuum evaporator which was separate from the cryostat, and at a pressure

FIGURE 6. DIAGRAM OF SAMPLE CONFIGURATION

of 2×10^{-5} torr.

In this configuration, it was found that the aluminum protects the alkali halide film very well. Samples were run, exposed to air for three months and the run repeated; the photoresponse was duplicated to within the experimental error. This would imply that during the short interval between removing the sample from the evaporator to the time it was mounted and the cryostat evacuated, there was negligible contamination.

F. Sample Holder and Cryostat

A schematic diagram of the sample holder is given in Figure 7. The ultraviolet radiation entered through the slit in the teflon cover A and brass disc B forming the front electrode and through the substrate C, striking the sample D. Motion of charge in the crystal induced a charge on the insulated aluminum film F which served as the rear electrode. Electrical connections were made by fine wires connected to the front electrode B and to the rear electrode F by a plunger assembly, which was insulated from the body of the holder by a teflon insulator H. The construction was such as to provide a guarded circuit. Thermal contact was made between the substrate and

FIGURE 7. DIAGRAM OF SAMPLE HOLDER

the body of the holder I which was mounted to the bottom of the inner cryostat reservoir.

Figure 8 shows the general arrangement of components in the cryostat. The sample holder was fixed to the bottom of the inner reservoir that was filled with liquid nitrogen or helium during the measurements. A polished copper radiation shield surrounded the sample holder and was connected to the inner container. Concentric to the inner reservoir was a liquid nitrogen reservoir with another radiation shield surrounding the first. All unused ports were blocked off to obtain maximum radiation shielding. The cryostat was separated from the rest of the system by means of a fused silica or LiF window, depending on the region of the spectrum studied. The window served a dual purpose; first, it isolated the cryostat vacuum system from the monochromator vacuum system and secondly, it served as a filter. Electrical connections were made to the sample via stainless steel tubing with a .020-inch diameter and a .005-inch wall. The tubing was mounted in quartz insulators fixed to the bottom of the outer radiation shield. One end of the tubing made contact with the brass fittings mounted in

FIGURE 8. DIAGRAM OF CRYOSTAT

quartz insulators which were cemented into the bottom of the cryostat. The other end of the tubing made contact with another set of brass fittings mounted in sapphire insulators which were fixed to the inner radiation shield. These fittings were connected to the sample electrodes by means of fine copper wires. Electrical contact was maintained between the tubing and the brass fittings through the spring pressure of the tubing upon the sides of the fittings. This type of contact permitted removal or rotation of the inner reservoir with electrical continuity established again upon replacement and alignment.

The temperature of the sample was measured by means of a calibrated Ag:Ag-Au:Co thermocouple which was affixed to the substrate.

G. Electronic Equipment

The detector used to measure the relative intensity of radiation on the sample was an RCA 941A photomultiplier and a sodium salicylate phosphor. The tube had an S-11 response which peaked in the blue region on the spectrum and very closely matched the sodium salicylate emission. The high voltage for the tube was supplied by a Fluke Model 403M regulated D.C. supply. The photo-

multiplier anode current was measured with a Keithley Model 414 micro-microammeter that had been modified to provide an output for Varian Model G-11 recording potentiometer.

Photocurrents were measured by a Cary Vibrating Reed Electrometer whose output was connected to the recording potentiometer.

The head of the electrometer had been modified to accomodate the high voltage connection to the cryostat. This connection was shielded from the sensitive electrode of the electrometer by a grounded brass partition. All electrical connections were rigid, hence they did not introduce microphonic behavior into the system. The voltage applied across the sample was supplied by highly insulated batteries that could be switched in such a manner as to provide a range in the applied voltage from -900 to +900 volts in 1-1/2-volt steps.

CHAPTER IV

EXPERIMENTAL PROCEDURE

A. General Techniques

The sample and aluminum films were evaporated on a substrate in a separate system as previously described. Immediately after evaporation, the sample was mounted in the sample holder and the cryostat evacuated as rapidly as possible to prohibit any undue contamination of the sample. When the cryostat was evacuated, the outer nitrogen container was filled to inhibit outgassing of the metal. This practice would also condense any vapors or other contaminants onto its surface rather than upon the sample. Liquid nitrogen or liquid helium was admitted into the inner reservoir after the pressure had been reduced to about 10^{-7} torr. and sufficient time had elapsed for the temperature of the outer container to reach equilibrium. The monochromator was also evacuated and the lamp and electronic equipment started. Stable operating conditions of the lamp and electronics were reached after a warm-up period of 45-60 minutes.

Alignment of the sample was obtained by rotation of the inner reservoir and sample holder to a predetermined

position. Prior to a run, with the sample removed, the holder was rotated into position and the mirror assembly adjusted to place the image of the monochromator exit slit in the center of the sample holder slit. This condition was obtained by using a microscope and viewing through the rear window of the cryostat with the monochromator set at zero order. With a sample mounted and after the cryostat and contained parts had obtained thermal equilibrium, proper alignment could be checked by setting the monochromator at zero order and again viewing the exit slit image through the microscope. To make this observation possible with the sample in place, the aluminum film over the sample was always made semi-transparent.

Because of the design of the monochromator, the incident angle of the output beam was a function of the wavelength of the emerging radiation. In the wavelength range from $800 \text{ \AA}$ to $3000 \text{ \AA}$ this angle varied from $8^{\circ}36'$ to $4^{\circ}51'$. Hence, if a small sample were placed some distance behind the exit slit such that the emerging beam would just fill the sample at one wavelength, at another wavelength the entire beam no longer struck the sample. This difficulty was eliminated by the use of a concave

mirror which imaged the exit slit on the surface of the sample. The diameter of the mirror was sufficiently large to insure the interception of the entire beam throughout the complete range of angle variation.

Several configurations and techniques were tried. For the measurement of photoconductivity in crystals, the scheme used by Nakai and Teegarden⁴⁰ was quite effective. It consisted of illuminating the sample transversely to the applied electric field and evaporating a KCl film of about $1000 \text{ \AA}$ over the surface to suppress external photoemission. Care was taken to assure that no part of the incident beam which was focused on the crystal, struck the electrodes and resulted in photoemission from the metal. This method was adequate only in the region of the spectrum where the KCl film was transparent. A criticism of this method is that in the region of the fundamental absorption, the absorption occurred within about $1000 \text{ \AA}$ of the surface. Hence photoelectrons were produced in this thin surface layer and were swept along the surface by the applied electric field. The effect measured was, therefore, largely a surface effect and not necessarily representative of the bulk of the material. The photocurrent as a function of photon energy as shown

by Nakai and Teegarden⁴⁰ is given in Figure 9. Our results, using their method, gave essentially a reproduction of this curve.

To measure the internal photoelectric effect in the bulk of the material, the crystal was illuminated through a transparent cathode. The cathode consisted of a fine copper mesh with a transmission of 63%. Again emission from the screen and crystal surface was suppressed by an evaporated layer of KCl, which also restricted measurements to the transparent region of the KCl.

Measurements were also made on thin films of the alkali halides. The configuration used consisted of a thin alkali halide film sandwiched between a LiF or fused silica substrate and an aluminum film. Held against the opposite side of the substrate was a brass disc, with a slit in the center, serving as the cathode. The substrate in combination with the brass disc constituted a blocking electrode and the aluminum film served as the anode. The ultraviolet radiation was focused and positioned carefully in the center of the slit to make sure that no light fell on any part of the sample holder that might give rise to photoemission. The beam then passed through the substrate onto the sample film. The

FIGURE 9. PHOTOCONDUCTIVITY IN RbI FROM NAKAI AND TEEGARDEN (40)

electrons freed by the light drifted into the film under the influence of the applied field. The field was developed by applying a voltage across the cathode and the anode. This motion of charge resulted in an induced charge on the electrodes which was detected and measured by the electrometer.

B. Suppression of External Photoemission

The fact that the alkali halide film was evaporated onto the substrate and illuminated through the substrate, made it highly improbable that any external photoemission from the sample could take place. For the films of any given material, the voltage at which saturation set in was always a linear function of the film thickness. Since photoemission would not show a dependence on thickness, this implies the current measured was a photoconductive current.

In order to further demonstrate that only photoconductivity was being observed, 0.1-mm crystals of RbI with the same geometry as the films were measured. If photoemission was important, the crystal would be expected to show saturation effects at about the same voltage as in the films. However, the photocurrents of

these crystals showed a linear dependence on the applied field over the region where the films show saturation effects. Figure 10 compares two RbI films of different thickness and a thin crystal in this region. Non-linear behavior of the photocurrents in the crystals began at fields in excess of 5×10^4 volts/cm.

For additional verification of the absence of photoemission, an auxiliary electrode was placed behind the sample, 1 cm from the cathode. A run was then made, repeating the measurement of the spectral response with the same magnitude of the electric field in the sample. If photoemission were the dominating contribution to the photocurrent, the signal should be essentially the same as in previous runs. In fact, the signal was diminished by a factor of 10 as expected. This was due to the change in the electrode spacing from 1 mm to 1 cm. Hence, a contribution to the measured photocurrent from photoemission can be ruled out.

The schubweg of an electron in the film and consequently the induced charge, was proportional to the applied field until the electron reached and was collected at the anode. Further increases in the applied field caused little increase in the induced charge. This

FIGURE 10. COMPARISON OF SATURATION CURVES OF RbI FILMS AND A THIN CRYSTAL.

effect was saturation. If the photocurrent was measured as a function of the applied voltage at constant intensity and photon energy, saturation was observed, as illustrated in Figure 10 in F-1 and F-2. This indicates a primary photocurrent, since primary currents are characterized by a saturation behavior with increasing electric field.

To observe this primary photocurrent, entrance of charge was controlled by the blocking electrode at the cathode resulting from the metallic electrode-substrate combination. The anode also provided a blocking electrode since the contact between most metals and any alkali halide is a blocking contact for both holes and electrons. This results from the fact that the valence band in alkali halides is 6-10 eV below the vacuum level and the Fermi level in most metals is about 4 eV below the vacuum level. Hence, at the anode there was a barrier of at least 2 eV to impede hole injection. The magnitude of this potential barrier may have been reduced somewhat by the influence of surface states and by the nature of the contact. The light intensity was sufficiently low that space charge limitations did not occur. This was demonstrated by the reproducibility of successive runs.

An interesting effect was noted if, for some reason, the pressure increased as high as 10^{-7} torr. Measurement of photocurrents of the order of magnitude of 10^{-15} amps was then impossible, due to the extremely high electrical drift of the system. This effect was not due directly to the increased pressure. If the cryostat pressure was allowed to increase with the ionization pump valved off, the electrical drift was normal. The drift was due to the increased ionization current within the vacuum pump. Some ions apparently migrated into the vicinity of the electrode and due to the sensitivity of the system their motion was detected. Consequently all measurements were made at pressures less than 5×10^{-8} torr. to circumvent this adverse effect.

C. Charge and Current Measurements

Measurement of the extremely small photocurrents was accomplished by the use of a vibrating-reed electrometer and the rate-of-charge method. The output voltage of the electrometer was related to the charge on the electrometer system by the expression $Q = EC$, where Q is the charge, E is the output voltage, and C is the electrometer capacitor with a stable capacitance of 10^{-11} farads.

In principle, the average current flowing into the electrometer could be determined from $I_{Av} = \frac{\Delta Q}{\Delta t}$ where ΔQ is the change in charge on the electrometer during the time Δt . However, it was necessary to correct for background currents of the electrometer arising from stresses in the insulators due to mechanical shock or temperature changes, ionization due to penetrating radiation, ionization due to alpha contamination, and surface leakage. The integrated charge pulse appeared on the recorder chart as a step in the trace of the pen. By averaging out the noise and graphically eliminating the effects of drift, the magnitude of the step could be quite accurately determined. Residual alpha contamination and other penetrating radiation occasionally caused bursts of ionization currents. These were evidenced by a sudden change in charge on the electrometer and consequently a very pronounced discontinuity in the record, easily distinguished from the signal step. These discontinuities caused by stray radiation could then be ignored. Figure 11 shows a typical signal step on the recorder chart. After the magnitude of the step was determined, the photocurrent was given by $i = \frac{\Delta v}{t} \times 10^{-11}$ amps, where Δv is

FIGURE II. TYPICAL RECORDER TRACE

the change in voltage represented by the step, 10^{-11} is the capacity in farads, and t is the time interval during which the sample was exposed to the ultraviolet radiation. Measuring the photocurrents in this way demanded that all measurements of photocurrent as a function of any variable be a point-by-point determination.

If the current exceeded 10^{-15} amps, the current could be measured directly by the steady deflection method. A high-value resistor was placed across the electrometer and the voltage output of the electrometer was related to the current in the circuit simply by $I = \frac{V}{R}$ where v is the output voltage and R is the resistance, in our case 9×10^{11} ohms. Using this method of measurement, the shutter was opened and remained open while the wavelength was scanned. The total time of irradiation when scanning was exactly the same as in the point-by-point measurements.

D. Spectral Response Measurements of Photoconductivity

The photocurrent was measured as a function of photon energy at a constant applied electric field. The magnitude of this field was always sufficient to saturate the photocurrent. The range of photon energy extended from below the exciton structure of the material to 10

electron volts. Both methods of current measurement were used depending on the magnitude of the signal. If the signal was large enough, greater than 10^{-15} amps, the steady deflection method was employed because it provided a continuous sampling of the response, thereby permitting random fluctuations to be averaged out or neglected.

Because of the intensity profile, the photocurrent at some photon energies was quite low; consequently, to provide a measurable signal, the minimum slit width was about 0.95 mm and the bandpass $38 \text{ \AA}$.

E. Saturation Measurements of Photoconductivity

The saturation data were taken on freshly evaporated films. After the film was mounted, the sample was heated to about 100°C for about 30 minutes by irradiating the sample holder with a 500-watt projector lamp. At this temperature the ionic conductivity was increased, resulting in a removal of any polarization that might be present and at the same time annealing the film to some extent.

With the sample mounted and the system evacuated as before, the monochromator was set at a given photon energy. The photocurrent was then measured as a function of the applied voltage at constant photon energy and intensity

using the rate-of-charge measurement current. The electrometer was always set at 10 millivolts for full-scale deflection, to provide the most sensitivity, as well as a good signal-to-noise ratio. The voltage was then increased in steps. At each point the exposure time was 10, 5 or 1 seconds; the longest interval was always used, with the constraint that the signal be within the 10-millivolt span of the electrometer and recorder. The data were then plotted and the theoretical saturation curve, derived previously, was fitted to provide a determination of the schubweg.

F. Intensity Measurements

Immediately after a run the phosphor was turned into the beam and the output of the micro-microammeter was connected to the chart recorder. The shutter was opened and the wavelength scanned at a speed of approximately 100 Å per minute. The scan was always made in the same direction, which was the same direction as the spectral response scan, to prevent any error in wavelength due to backlash. For convenience in data reduction, markers were placed on the record at every 0.1 electron volt rather than in angstrom units.

The relative intensity measurement was then corrected for the response of the sodium salicylate. Usually the response of the phosphor is assumed to be flat over the region of photon energies used. But recent experiments performed by Kristianpoller and Knapp⁴⁷ indicate that there is a small dip or step in the quantum yield of sodium salicylate in the region around 2000 Å which corresponds to photon energies in the neighborhood of 6 ev. Figure 12 shows their data for the quantum yield of sodium salicylate as a function of photon energy.

A linear correction to the measured photocurrent was made for the variation of intensity with photon energy. Figures 13 and 14 show that the photocurrent is a linear function of intensity over this range of variation. The intensity was always normalized relative to the intensity at a given photon energy for each material, hence at that value, the current plotted was the true measured photocurrent. This practice allows direct comparison between the curves taken for various samples.

An absolute measure of the light intensity was obtained by calibrating an EMI 6097S photomultiplier-sodium salicylate combination against a thermocouple used

FIGURE 12. YIELD OF SODIUM SALICYLATE FROM KRISTIANPOLLER AND KNAPP (47)

FIGURE 13. PHOTOCURRENT AS A FUNCTION OF INTENSITY FOR RbI.

FIGURE 14. PHOTOCURRENT AS A FUNCTION OF INTENSITY FOR KCl

as a secondary standard. The calibration was performed at photon energies below about 6.0 ev. Measurements of intensity at higher energies were made by using the phosphor response curve shown in Figure 12.

G. Measurements of Film Thickness

Thickness measurements were facilitated by the aluminized surface presented by the aluminum film electrode. A microscope slide selected for flatness was coated with a semi-transparent aluminum film. The slide was placed over the sample with the aluminized surfaces together. This formed an air wedge and when illuminated with the 5460 Å mercury line, produced Fizeau fringes. These fringes were photographed and the fringe shift, produced by the change in elevation caused by the alkali halide film under the aluminum film, was measured. The displacement of the fringe could be measured to about one tenth of a fringe or $1/20$ of a wavelength.

CHAPTER V

DESCRIPTION OF RESULTS

A. Spectral Response of Photoconductivity

Spectral response measurements of all the materials were taken at liquid nitrogen and liquid helium temperatures. The slit width was 0.95 mm corresponding to a band pass of 38 Angstroms. Measurements were made using the constant deflection method in cases where the signal exceeded 10^{-15} amps. A run would be started using the rate-of-charge method until the current increased, then the steady deflection method would be used for the remainder of the run. The response measured with each method yielded identical results.

There has been no correction made for reflectivity since reflectivity measurements could not be made on this apparatus. Reflectivity data taken by other investigators are incompatible with our data because of the wide band pass that was necessary for our work. A discussion in the next chapter will show that some of the structure observed is not a result of reflectivity variations.

Since the spectral response data were taken with a sufficiently high applied field to always saturate the

photocurrents, the spectral response curves reflect the dependence of $\eta_a(1-R)$ on the incident photon energy. The absolute value of $\eta_a(1-R)$ was obtained from saturation data for only one value of photon energy. Since the spectral response curves have been normalized to that photon energy, they give absolute values of $\eta_a(1-R)$ for other photon energies in the range covered. The photocurrents were also corrected for variations in the intensity of the stimulating radiation.

1. Rubidium Iodide

The spectral response of RbI at 80°K is given in Figure 15 in which the photocurrents have been normalized to the intensity and absolute value of $\eta_a(1-R)$ at 6.55 ev. These results are of a RbI film evaporated on a fused silica substrate. The main feature is the sharp rise in the photocurrent of about two 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.

There appears an inflection point on the rising photocurrent at about 6.25 ev which is near the second

FIGURE 15. SPECTRAL RESPONSE OF RbI at 80° K.

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.

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 can not be resolved and consequently show up as only one minimum. There also appears to be a photoconductivity peak 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 of the first fundamental peak and to be associated with the β -band or other defect centers.

The spectral response of the photoconductivity at 10°K is given in Figure 16. 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 is still difficult to detect but remains on the high-energy side of the first fundamental absorption peak. It is possible that this peak may be associated with the second component of the exciton doublet, analogous to the association of the β -band to the first component.

2. Potassium Bromide

The spectral dependence of the photoconductivity in a film of KBr at 80°K is shown in Figure 17. This film was deposited on a LiF substrate. The curve shown was normalized to the absolute value of $\eta_a (1-R)$ at 8.6 ev. These data have also been corrected for variation in the intensity of the stimulating radiation. In KBr both components of the spin-orbit doublet are at

FIGURE 16. SPECTRAL RESPONSE OF RbI at 10° K.

FIGURE 17. SPECTRAL RESPONSE OF KBr at 80° K.

lower energies than the "step" in the optical absorption spectrum. The response curve shows peaks which are dependent on the history of the irradiation and are located at the positions of each fundamental absorption band. A dashed curve indicates the growth of the peaks after the sample was irradiated 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 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 in 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 Figure 18. This 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 had 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

FIGURE 18. SPECTRAL RESPONSE OF KBr at 10° K.

other features. The structure is also sharper at this lower temperature than it was in the case of RbI.

3. Potassium Chloride

Photoconductivity as a function of photon energy at 80°K is given in Figure 19 where the current has been corrected for intensity variation relative to 9.6 ev. The data have also been normalized to the absolute value of $\eta_a(1-R)$ at 9.5 ev. 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. 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 20 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

FIGURE 19. SPECTRAL RESPONSE OF KCl at 80° K.

FIGURE 20. SPECTRAL RESPONSE OF KCl at 10° K.

photon energies corresponding to the spin-orbit doublet. This is illustrated in the insert in Figure 19. 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.

4. Rubidium Chloride

In addition to the preceding data, the spectral dependence of the photoconductivity of RbCl was measured only at 80°K. These measurements were also taken on a thin film evaporated on a LiF substrate. Figure 21 shows the spectral response which has been normalized to the intensity measured at 9.5 ev. This dependence on photon energy is similar to that of the other alkali halides previously discussed. In addition to the peak near the fundamental absorption bands, there appears some indication of another at the position of the second large band in the optical absorption spectrum. The nature of the peak near the fundamental absorption was not investigated, but it most likely shows the same dependence on previous ultraviolet irradiation as did the corresponding peak in the other alkali halides studied.

FIGURE 21. SPECTRAL RESPONSE OF RbCl at 80° K.

The photocurrent is down by over an order of magnitude at 8.0 ev and begins to rise rapidly, showing what appears to be a small peak at about 6.25 ev. Then the current continues to rise into a peak at the position of the second large absorption band.

B. Saturation of Photoconductivity

The films used to measure saturation of the photoconductive currents were sufficiently thick so that all of the incident radiation was absorbed. With the thicknesses used and with the absorption coefficient between 10^5 and 10^6 cm^{-1} , the theoretical saturation curve could be used in the limit as $\alpha \rightarrow \infty$. The resulting formula for the saturation curve is that given by Hecht.³⁵

$$\psi = \frac{\omega}{\ell} (1 - e^{-\ell/\omega})$$

Reiterating the relationship between the pertinent quantities:

$$i = e \eta_a N_o (1 - R) (1 - e^{-\alpha \ell}) \psi$$

where i is the photocurrent, η_a is the quantum efficiency per absorbed photon, N_o is the number of incident photons per second, and ψ is the saturation factor.

Also the relationship for ω is $\omega = \omega_o E$ or $\omega = \omega_o \frac{V}{d_{\text{eff}}}$ where ω_o is the range per unit field, V the

applied voltage and d_{eff} is the effective separation of the electrodes. d_{eff} takes into account the difference in the dielectric constants of the substrate and the film and is given by $d_{eff} = (l - \frac{\epsilon_f}{\epsilon_s} d)$ where l and ϵ_f are the thickness and dielectric constant of the film and d and ϵ_s are the thickness and dielectric constant of the substrate. It was assumed that the dielectric constant of the alkali halide film is the same as that of the material in its crystalline form.

The photocurrent is directly proportional to the saturation factor ψ since these measurements are made at constant intensity and photon energy. We have assumed ω_0 to be field-independent, hence the schubweg is proportional to the applied voltage. As a result of these two conditions, the data can be fitted directly with the theoretical curve. To determine the range per unit field (ω_0), one needs only to pick a value of ω/l and find the corresponding voltage. As an example take $\omega/l = 1$ which corresponds to the voltage, say V_1 , then ω_0 is given by

$$\omega_0 = d_{eff} \frac{l}{V_1} = \frac{dl}{V_1} \left(\frac{l}{d} + \frac{\epsilon_f}{\epsilon_s} \right).$$

With the additional measurement of the photon flux, N_0 , the quantity $\eta_a (1-R)$ is given by

$$\eta_a (1-R) = \frac{L}{e N_0 (1 - e^{-\alpha L}) \psi} .$$

1. Rubidium Iodide

Figures 22 and 23 present the saturation data taken at 80°K of two films of RbI with thicknesses of 680 Å and 2960 Å, respectively. The curves of these two films have been compared to that of a crystal 0.1 mm thick, previously, in Figure 10. Saturation data for the films were obtained at a photon energy of 6.5 ev and those for the crystal at 6.5 and 7.3 ev. The relatively large data scatter is due to the low lamp intensity in this region of the spectrum. Fitting the theoretical curve to these data yields a value of $\omega_o = 2.58 \times 10^{-8} \text{ cm}^2/\text{volt}$ for F-1 and $\omega_o = 2.80 \times 10^{-8} \text{ cm}^2/\text{volt}$ for F-2. The photon flux at 6.5 ev was 6.8×10^{10} photons/sec and $\eta_a (1-R)$ was 0.06.

2. Potassium Bromide

The saturation curves for KBr were taken at 80°K and at a photon energy of 8.6 ev. Figures 24 and 25 show the theoretical curve fit to these data for films of thicknesses 1090 Å and 2460 Å, respectively. Values

FIGURE 22. SATURATION CURVE FOR RbI at 80°K.

FIGURE 23. SATURATION CURVE FOR RbI at 80°K.

FIGURE 24. SATURATION CURVE FOR KBr at 80° K.

FIGURE 25. SATURATION CURVE FOR KBr at 80°K.

obtained for the schubweg per unit field are 1.33×10^{-8} cm^2/volt for F-17 and 1.29×10^{-8} cm^2/volt for F-18. The sensitivity of the fit is illustrated in Figure 24 by the two dashed curves representing $\omega_0 \pm 0.2 \times 10^{-8}$ cm^2/volt . The quantity $\eta_a(1-R) = 0.11$ at 8.6 ev with an incident photon flux of 6.3×10^{10} photons/sec.

3. Potassium Chloride

The saturation data taken at 80°K of KCl are shown in Figures 26 and 27. Both curves were taken at a photon energy of 8.6 ev with the only difference being the thickness of the two films. F-19 shown in Figure 24 is 3820 Å thick and F-20 shown in Figure 25 is 9060 Å in thickness. Fitting the theoretical curve to the data as before gives a value of $\omega_0 = 1.97 \times 10^{-7}$ cm^2/volt for F-19 and $\omega_0 = 2.02 \times 10^{-7}$ cm^2/volt for F-20. This longer unit range is made evident by the low voltage at which saturation sets in. The photon flux was again equal to 6.3×10^{10} photons/sec yielding a value for $\eta_a(1-R)$ of 0.033 at 6.8 ev.

FIGURE 26. SATURATION CURVE FOR KCl at 80°K.

FIGURE 27. SATURATION CURVE FOR KCl at 80°K.

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY

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

A. Rubidium Iodide

At 80°K, the quantity $\eta_a(1-R)$ 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 Teegarden⁴⁰ also observed this decrease in the photocurrent in the first absorption band. They 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.¹⁹ This change in the reflectivity is insufficient to account for the minimum which occurs. This result suggests that a competing process is taking place between non-photoconducting transitions and inter-band 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 fundamental absorption band is down by nearly two orders of magnitude from its maximum value, supports the concept of the formation of non-conducting states at these energies.

As mentioned previously, Fischer and Hilsch⁸ have shown from optical absorption measurements that there is a peak on the "step" in the optical absorption spectrum of RbI. Figure 28 shows the optical absorption spectrum of RbI at 80°K measured by Baldini.⁹ These data emphasize the region of the "step" and show two peaks on the "step" at 6.09 eV and 6.23 eV. The positions of the spin-orbit components are indicated by arrows at 5.70 eV and 6.47 eV. At 10°K these peaks on the "step" are more pronounced and are shifted to 6.12 eV and 6.26 eV, respectively. The absorption spectrum at 10°K is shown in Figure 29. The

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 fundamental absorption band is down by nearly two orders of magnitude from its maximum value, supports the concept of the formation of non-conducting (bound) states at these energies.

As mentioned previously, Fischer and Hilsch⁸ have shown from optical absorption measurements that there is a peak on the "step". Figure 28 shows the optical absorption spectrum of RbI at 80°K measured by Baldini.⁹ These data emphasize the region of the "step" and show two peaks on the "step" at 6.09 and 6.23 ev. The positions of the spin-orbit components are indicated by arrows at 5.70 and 6.47 ev. At 10°K these peaks on the "step" are more pronounced and are shifted to 6.12 and 6.26 ev, respectively. The absorption spectrum at 10°K is shown in Figure 29. The position of the spin-orbit doublet is again shown by the arrows at 5.71 and 6.48 ev.

A comparison of the spectral response of RbI at 80°K to the optical absorption measured at this temperature shows that the photocurrent in the small absorption band at 6.09 ev, which is the band on the leading edge

FIGURE 28. ABSORPTION SPECTRUM OF RbI
AT 80°K. from BALDINI (9)

FIGURE 29. ABSORPTION SPECTRUM OF RbI
AT 10° K. from BALDINI (10)

position of the spin-orbit doublet is again shown by the arrows at 5.74 ev and 6.49 ev. These peaks have been interpreted as the components of a Wannier exciton series.⁸

A comparison of the spectral response of RbI at 80°K to the optical absorption measured at this temperature 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 and the photocurrents have diminished to about two orders of magnitude relative to their maximum value. This suggests that the absorption band at 6.09 ev may also be a result of the formation of a non-conducting 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. At this photon energy $\eta_a(1-R)$ has a value of 0.05 and the photocurrent is down by a factor of about three 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 $\eta_a(1-R)$ 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 $E_{\text{act.}}$ is the activation energy, then $.0067 \text{ ev} > E_{\text{act.}} > .0008 \text{ ev}$.

Assuming that the first three peaks in the optical absorption spectrum are Wannier-type excitons as suggested by Fischer and Hilsch⁸, the ionization limit may be calculated using the relationship $h\nu = E_0 - \frac{G}{n^2}$ where E_0 is the ionization energy, G is the binding energy of the exciton and $n = 1, 2, 3 \dots$. Neglecting 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 ev 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.

The small measured photocurrents in the vicinity of the first fundamental band increased with prolonged irradiation. These currents can be reduced by bleaching or heating the sample. Nakai and Teegarden⁴⁰ observed that the

photocurrents in this region appeared to increase as the square of the intensity, implying that a secondary process may be involved. It is believed that these small photocurrents stimulated by absorption in the first fundamental band result from the photoproduction and destruction of color centers.

An interesting comparison to make is that of $\eta_a(1-R)$ and the quantum efficiency of photoemission at 7.0 ev. At this photon energy $\eta_a(1-R)$ is about 0.23 and the quantum efficiency of emission from Figure 2a is less than 10^{-3} . This is further evidence that over the range of photon energies employed that only photoconductivity was being observed in the sample.

B. Potassium Bromide

The interpretation of the results of KBr 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.

In KBr the photocurrent measured at 80°K shows

what might be a small peak at about 7.9 ev, as compared to the edge of the "step" at 7.8 ev. But at 10°K, the photocurrent appears smooth over this region. This behavior is very similar to that observed in RbI. It is possible that the "step" observed in KBr also is composed of several absorption peaks and at 10°K the ionization of some of the excited states is thermally quenched.

There is a small peak at 8.3 ev in the optical absorption spectrum of KBr at 80°K, shown in Figure 1. It is interesting to note that the energy separation between this peak and the "step" is the same as the splitting of the spin-orbit doublet. Also, the energy difference between the first spin-orbit component and the "step" is very nearly equal to the difference between the photon energies corresponding to the second spin-orbit component and this small peak at 8.3 ev. In the light of recent detailed optical absorption spectra of the iodides⁸, and in particular RbI⁹ discussed above, one might expect that the "step" of KBr, also, consists of a series of absorption bands corresponding to the formation of higher excited states associated with the first component of the spin-orbit doublet. It is possible that the peak at 8.3 ev

corresponds to the second line of a series associated with the second component of the doublet.

As a result of the presence of additional structure in the region, inter-band transitions are expected and the lack of detailed optical absorption data makes a determination of the band-gap energy in KBr very difficult. As discussed in the case of RbI, the value of the band gap corresponds to the ionization limit of the Wannier exciton series.

If the step in the absorption spectrum of KBr is due to such a series, we can estimate the ionization limit by comparison with the corresponding series in RbI. This leads to an estimate of 8.0 eV for the band gap of KBr.

C. Potassium Chloride and Rubidium Chloride

The photocurrents in KCl and RbCl show the same general features. Interpretation of the data is complicated, as it was in KBr, by the lack of detailed absorption data. The situation is further complicated by the fact that the spin-orbit doublet in the optical absorption shows a splitting of 0.11 and 0.13 for KCl and RbCl, respectively. As a result, it is likely that the structure due to higher excited states may overlap in the

region of the "step". The photocurrents appear to show a slight increase in magnitude over this region but any structure present is not resolved.

Estimating the band gap in these materials by comparing the optical absorption curves to that of RbI, as discussed above, gives a value of about 8.9 ev for the band gap in KCl and about 8.5 ev in RbCl.

The preceding results can be summarized in the following table.

Sample	$\eta_a(1-R)_{\max}$	E_g in ev	E_s in ev	E_1 in ev	E_2 in ev	ω_0 in cm^2/volt
RbI	0.22	6.36	6.1	5.70	6.47	2.7×10^{-8}
	0.11*	6.37	-	5.74*	6.49*	
KBr	0.32	8.0	7.8	6.77	7.26	1.3×10^{-8}
	0.19*					
KCl	0.38	8.9	8.5	7.76	7.87	2.0×10^{-7}
	0.22*					
RbCl		8.5	8.2	7.51	7.64	-

The symbols employed above are as follows: * represents data taken at 10°K; $\eta_a(1-R)_{\max}$ is the maximum value of the product of the quantum efficiency per absorbed photon and one minus the reflectivity; E_g is the

band-gap energy; E_s is the photon energy of the "step" taken from earlier optical absorption measurements; E_1 and E_2 are the photon energies at the first and second components of the spin-orbit doublet, and ω_0 is the range per unit field.

D. Suggestions for Further Investigations

The threshold for photoconductivity in KBr, KCl and RbCl is not extremely sharp, as it is in the case of RbI, consequently the assignment of an energy to the onset of inter-band transitions is somewhat less precise. Since defects are removed and the structure is improved in thin films upon annealing, the optical properties of an annealed thin film more closely approximate those of a perfect crystal. The usual effect observed is an improvement in the structural quality which makes small effects more pronounced. It would be of interest to measure the spectral dependence of the photocurrents on well-annealed thin films with higher resolution than that used in our work. Also, these measurements should be performed on films with carefully measured optical absorption spectra.

Mixed crystals appear to provide a good system in which to study exciton structure. Preliminary experiments

using about one per cent of RbI in RbCl have shown three absorption bands corresponding to the so-called first Wannier series in pure RbI and the second component of the spin-orbit doublet in RbI.⁵¹ This structure is in the transparent region just preceding the first fundamental absorption band of RbCl. Preliminary measurements show photocurrents which may be due to ionization of the I^- ion. Additional measurements of photoconductivity and absorption in well annealed films may show that these currents are large at the ionization limit of the Wannier series.

The mobility and the unit range are of interest as a result of their intimate connection with both the scattering and trapping mechanisms. If measurements of these quantities are performed as a function of temperature, some insight into the nature of the traps, as well as the scattering mechanism, might be established.

One possible method measuring the unit range and mobility is discussed by Hofstadter⁴⁹ in connection with crystal counters and employed by Brown⁵⁰ in studying AgCl. This method consists of irradiating a crystal or, in our case, a thin film, with β -rays and measuring the transit

time. A saturation curve can then be obtained by measuring the pulse height as a function of the applied field. From the saturation curve a value for the unit range is obtained in the same way as that employed in this work. From the value of the unit range and the measured transit time one can then determine the drift mobility. Similar measurements can be performed using α particles, γ -ray or X-ray radiation to simulate photoconductivity.

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