rated by the fact that the experimental results on the electronic $g$-value of the Mn ions and the Knight shift of the Cu-nuclei can be qualitatively accounted for.

However, there still remain difficult problems concerning the properties shown by Cu-Mn alloys. The important one is that of the antiferromagnetic transition. The writer believes that the essential interaction between Mn spins is the Ruderman-Kittel interaction. A difficulty lies in the statistical problem concerning the dilute and randomly distributed spin system. Another difficulty which is more essential is in calculating the actual $\mathbf{q}$-dependence of $J(\mathbf{q})$. The positive paramagnetic Curie temperature and the occurrence of the antiferromagnetic ordering may be explained by the special $\mathbf{q}$-dependence of $J(\mathbf{q})$.

## ACKNOWLEDGMENTS

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# Photoconduction in KBr and KI Containing *F* Centers*

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Photoconductivity in potassium bromide and potassium iodide containing $F$ centers has been investigated at 80°K. The product of the quantum yield and unit range has been measured over the spectral range from 2.0 to 5.8 ev with $F$-center concentrations between $10^{16}$ and $10^{17}$ cm$^{-3}$. Evidence is presented that the mechanism for the production of photoelectrons depends upon the photon energy and the concentration of $F$ centers. Two mechanisms for the production of photoelectrons are suggested by the data: the ionization of $F$ centers by excitons and direct optical ionization of $F$ centers.

## INTRODUCTION

THE pure alkali halides do not exhibit photoconductivity but the absorption of photons by $F$ centers in these crystals excites an internal photocurrent.[1,2] Taft and Apker have shown that the absorption of photons by the first fundamental band which lies near 2000 A will yield *photoemission* from the alkali halides *if F centers are present*.[3] It appears that photon absorption by the first fundamental band produces an excited nonconducting state of the crystal and that the excitons can ionize $F$ centers.

These experiments suggest that *photoconductivity* occurs in alkali halides containing $F$ centers on irradiation in the first fundamental absorption band. The present experiments investigate the dependence of this process on the energy of the absorbed photon and the concentration of $F$ centers. Additional information has been obtained concerning the origin of the photoconductivity excited by irradiation in the spectral region occupied by the high-energy tail of the $F$ band.[4]

## MATERIALS

Potassium bromide and potassium iodide crystals were obtained from the Harshaw Chemical Company. Potassium iodide crystals were also grown by the Kyropoulos method from Baker's Analyzed Grade of the salt. Thallium absorption bands at 285 and 236 mμ were observed in the Harshaw potassium iodide at 80°K. The concentration of thallium was estimated as approximately one part per million. The thallium absorption bands were not detectable in the home grown potassium iodide crystals. The photoconductive behavior of the two types of potassium iodide crystals was similar.

## *F*-CENTER PREPARATION

$F$ centers were prepared by heating the crystals for 12 hours in potassium vapor. The temperature of the crystals was 570°C and the desired vapor pressure of potassium was obtained by maintaining the tempera-

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* Partially supported by the Office of Scientific Research, U. S. Air Force and the Office of Naval Research, Department of the Navy.

[1] A. Smakula, Z. Physik **63**, 763 (1930).

[2] N. Mott and R. Gurney, *Electronic Phenomena in Ionic Crystals* (Oxford University Press, New York, 1940), Chap. IV.

[3] E. Taft and L. Apker, Phys. Rev. **79**, 964 (1950); **81**, 698 (1951); **82**, 814 (1951); **83**, 479 (1951); J. Chem. Phys. **20**, 1648 (1952).

[4] J. Oberly and E. Burstein, Phys. Rev. **79**, 905 (1950).

ture of the potassium metal between 250°C and 400°C. The crystals were sealed in an evacuated Pyrex tube. The potassium metal was vacuum distilled into the Pyrex tube after several preliminary vacuum distillations.

The potassium iodide crystals were wrapped in aluminum foil, heated to 420°C for 5 minutes, and quenched to room temperature in carbon tetrachloride before any measurements were made. This treatment was necessary to remove colloids which were present in the potassium iodide crystals after the introduction of *F* centers. *F* centers are unstable in potassium iodide at room temperature, and aggregate to form colloids in a time of the order of a few hours.

*F* centers are quite stable in potassium bromide at room temperature and no special heat treatment was necessary to remove colloids. No trace of optical absorption due to colloids was found after additive coloration in potassium vapor. A typical *F* absorption band is shown in Fig. 1. The *F* band and the colloid band in the potassium iodide crystals was similar to that observed by Scott.[5]

For photoconductivity measurements the crystals were cleaved to dimensions of approximately 13×14 ×1 mm.

## OPTICAL ABSORPTION

The concentration of *F* centers was determined by measuring their optical absorption and using Smakula's equation[6] in the form

$$c_F = 1.31\times10^{17}\left(\frac{n_0}{(n_0{}^2-2)^2}\right)K_m H, \qquad (1)$$

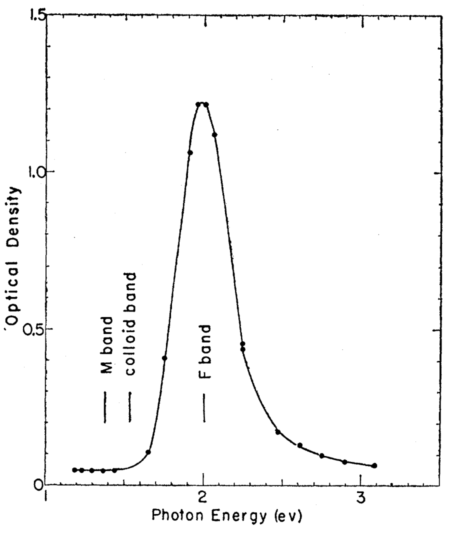

FIG. 1. The *F* band in KBr at room temperature. Crystal thickness 0.71 mm; $c_F = 1.6\times10^{17}$ cm$^{-3}$. The accepted locations of the *F*, *M*, and colloid bands are indicated.

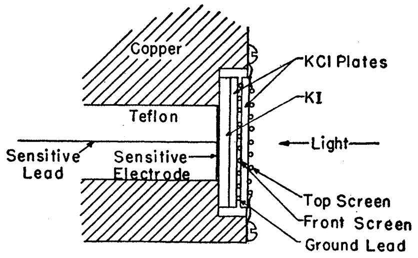

FIG. 2. Crystal mount.

where $c_F$ is the concentration of *F* centers in cm$^{-3}$; $n_0$ is the index of refraction of the crystal at the wavelength of the maximum of the *F* band; $K_m$ is the absorption constant in cm$^{-1}$ at the maximum of the *F* band; *H* is the half-width of the *F* band in electron volts. For potassium iodide at room temperature, $H = 0.38$ ev and $n_0{}^2 = 2.69$. For potassium bromide at room temperature $H = 0.36$ ev and $n_0{}^2 = 2.33$.

The optical absorption of the crystals was measured at room temperature with a Cary recording spectrophotometer and Beckman D and DU instruments. Optical absorption measurements at liquid nitrogen temperature were made with a Leiss double monochromator. An Eastman Kodak lead sulfide cell was used as a detector in the near infrared.

## PHOTOCONDUCTIVITY MEASUREMENTS

The photoconductivity of potassium bromide crystals in the visible region of the spectrum was investigated by using a Beckman D instrument as a monochromator. The radiation source was a tungsten lamp and the number of photons per second incident upon the crystal was determined with a calibrated photocell. The absolute spectral distribution curve of this cell (electrons/quantum *vs* wavelength) was determined by comparison of its response with that of a Perkin-Elmer radiation thermocouple which had been calibrated with a standard lamp.

For photoconductivity measurements in the ultraviolet region of the spectrum, a Farrand single monochromator with crystal quartz prisms was used to disperse the radiation from a Hanovia quartz hydrogen lamp. The entrance and exit slits of this instrument were set at 1 mm width which yielded a band pass of 1 m$\mu$ at 200 m$\mu$ and 10 m$\mu$ at 300 m$\mu$. The number of photons per second incident upon the crystal was determined with a calibrated cesium-antimony cell. The number of photons per second incident upon the crystal varied from about $10^{12}$ at 400 m$\mu$ to $10^{10}$ at 220 m$\mu$.

Photocurrents in the crystals and photocells were amplified by an Applied Physics Laboratory Vibrating Reed Electrometer and recorded by an Esterline-Angus milliammeter. The input grid resistor of the electrometer was $10^{10}$ ohms. The electric field applied to the crystal

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[5] A. B. Scott, J. Phys. Chem. **57**, 757 (1953); A. B. Scott and L. P. Bupp, Phys. Rev. **79**, 341 (1950).

[6] A. Smakula, Z. Physik **59**, 603 (1930).

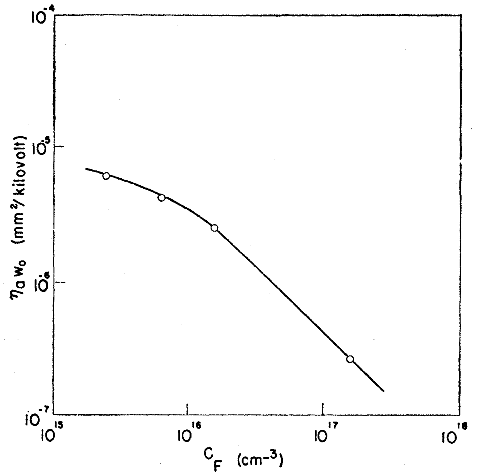

FIG. 3. $\eta_a w_0$ *versus* $c_F$ in KBr at 80°K. Photon energy =2.02 electron volts.

was obtained with dry cells. This field was between 1000 and 10 000 volts/cm.

The crystal was illuminated for a time of 10 seconds during a measurement of the photocurrent. Each measurement was repeated with reversed electric field to insure that the polarization of the crystal was negligible. The measured photocurrent was less than $10^{-13}$ ampere and the charge released in the crystal was of the order of $10^{-12}$ coulomb in each measurement.

Photoconduction experiments with photon energies greater than 4 electron volts are made difficult by a variety of spurious photocurrents. Photoemission may occur from the metal electrodes or from the crystal surface into the vacuum of the cryostat. Photoemission may also occur into the crystal from the electrodes. These effects make difficult the design of a satisfactory crystal mount. The crystal mount which was used in these experiments is illustrated in Fig. 2. The crystal mount was fastened to the bottom of the liquid nitrogen container of the cryostat.[7]

The sensitive electrode which was connected to the electrometer input was 8 mm in diameter and mounted in a teflon cylinder of 9 mm diameter which was press fitted into the copper block of the crystal mount. The electrical lead from this electrode was carefully shielded from radiation and electrical charge within the cryostat. The surface of the sensitive electrode was covered with a thin layer of G. E. resin 7031 to prevent photoemission into the crystal from the electrode by radiation transmitted through the crystal.

The grounded electrode was an oxidized nickel screen of 0.003-in. diameter wire and 80 mesh. To prevent microphonics and to insure a uniform field, this screen was sandwiched between a pair of potassium chloride crystals. A second grounded nickel screen was held against the outer potassium chloride crystal by leaf springs of beryllium copper. The optical transmission of the pair of nickel screens was approximately 50%.

Direct measurement of the crystal temperature with an embedded thermocouple showed that the crystal temperature was within 10°K of the temperature of the liquid nitrogen.

When the crystal was cooled with liquid nitrogen the electrical noise at the output of the amplifier corresponded to a random input current of $2\times10^{-15}$ ampere. The photoconduction currents in potassium bromide and iodide crystals containing no $F$ centers were below this noise level over the entire spectrum of photon energies used in these experiments.

The photocurrent, $i$, when $N$ quanta per second are incident upon a crystal which forms the dielectric of a plane parallel condenser, is given by the equation

$$i=(\eta w_0)eVN/d^2 \tag{2}$$

if the electron range, $(w_0V/d)$, is much less than $d$, the separation of the electrodes. $\eta$ is the quantum yield, the number of conduction electrons produced per incident quantum and $w_0$ is the unit range, the displacement of a photoelectron in the field direction by unit electric field. At the temperature used in these experiments, photoelectrons are trapped by $F$ centers to form $F'$ centers. $V$ is the potential difference applied to the electrodes. $e$ is the electronic charge. It was not possible, unfortunately, to determine the fraction of the incident photons which were absorbed by the crystal because of the small absorption coefficient over most of the spectral range investigated. An exception to this statement occurred in the case of photocurrents excited by absorption of photons near the maximum of the $F$ band where the absorption coefficient was measured. In this case, it was possible to determine $\eta_a w_0$ from the measurements. $\eta_a$ is the number of photoelectrons produced per absorbed quantum.

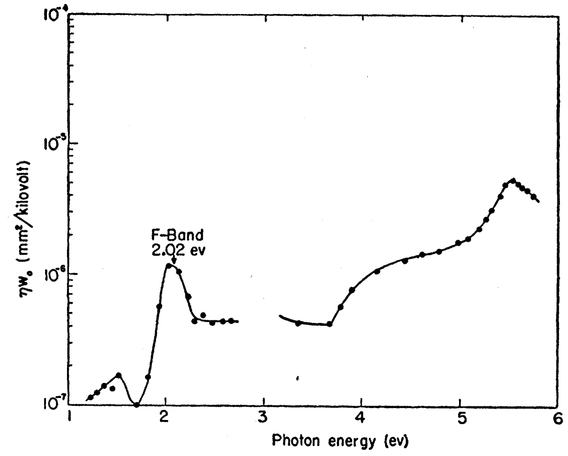

FIG. 4. $\eta w_0$ *versus* photon energy in KBr at 80°K. Low-energy data from crystal 1.29 mm thick with $c_F=1.49\times10^{16}$ cm$^{-3}$. High-energy data from crystal 1.23 mm thick with $c_F=1.42\times10^{16}$ cm$^{-3}$.

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[7] D. B. Dutton and R. J. Maurer, Phys. Rev. **90**, 126 (1953).

A minor alteration of Eq. (2) was necessary in the present experiments where a crystal of potassium chloride was interposed between the grounded electrode and the crystal of potassium bromide or iodide. In this case,

$$d=\left(d_1+d_2\frac{\epsilon_1}{\epsilon_2}\right), \tag{2a}$$

where $d_1$ and $\epsilon_1$ are the thickness and dielectric constant of the potassium bromide (or iodide) crystal and $d_2$ and $\epsilon_2$ are the thickness and dielectric constant of the potassium chloride crystal.

It has been established by Pohl[8] that the unit range of photoelectrons, $w_0$, is inversely proportional to $c_F$, the concentration of $F$ centers in KCl, at $-100°$C within a range of concentrations from slightly greater than $10^{15}$ cm$^{-3}$ to $10^{18}$ cm$^{-3}$. This result is excellent evidence that the photoelectrons are trapped by $F$ centers. A test of this dependence of $w_0$ on $c_F$ was made on the potassium bromide crystals used in the present investigation. The results are shown in Fig. 3 where the straight line portion of the curve represents an inverse proportionality of $\eta_a w_0$ and $c_F$. Since $\eta_a$ is believed independent of $c_F$, this data leads to the conclusion that $w_0$ is inversely proportional to $c_F$ for $F$ center concentrations greater than $10^{16}$ cm$^{-3}$. The decrease in slope of the curve for $F$ center concentrations smaller than $10^{16}$ cm$^{-3}$ is probably the result of electron trapping by centers other than $F$ centers.

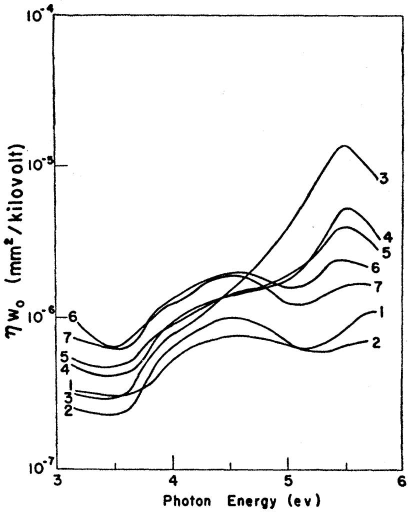

FIG. 5. $\eta w_0$ *versus* photon energy in KBr at 80°K. See Table I for data pertaining to each curve.

This data is in poor agreement with the results of Glaser and Lehfeldt on $\eta_a w_0$ as a function of temperature in potassium bromide containing $1.6\times10^{16}$ cm$^{-3}$ $F$ centers.[9] Glaser and Lehfeldt's value for $\eta_a w_0$ at 80°K is approximately 30 times greater than the present value.

TABLE I. Data pertaining to Fig. 5.[a]

| Curve No. | $d$ (mm) | $c_F$ (cm$^{-3}$) |
|---|---|---|
| 1 | 1.38 | $2.5\times10^{15}$ |
| 2 | 1.47 | $6.5\times10^{15}$ |
| 3 | 1.33 | $9.3\times10^{15}$ |
| 4 | 1.23 | $1.4\times10^{16}$ |
| 5 | 1.32 | $5.9\times10^{16}$ |
| 6 | 1.14 | $1.9\times10^{17}$ |
| 7 | 1.22 | $2.6\times10^{17}$ |

[a] $d$ = crystal thickness; $c_F$ = concentration of $F$ centers.

## POTASSIUM BROMIDE

The spectral distribution of the photocurrent in potassium bromide containing $F$ centers is shown in Fig. 4. Between 1.0 and 2.0 ev, there is a small maximum of $\eta w_0$ due to $F'$ centers that were accidentally present. At approximately 2.0 ev the maximum in $\eta w_0$ due to the $F$ band occurs. For photon energies greater than 3.7 ev, $\eta w_0$ rises and passes through a maximum near 5.5 ev. Evidence will now be presented that the photocurrent observed in the vicinity of 4.0 ev is due to direct ionization of $F$ centers by photons absorbed by $F$ centers and that the photocurrent observed near 5.5 ev is due to the absorption of photons by the crystal with the formation of excitons which transfer their energy to the $F$ centers and ionize them.

Figure 5 shows the spectral distribution of $\eta w_0$ between 3.0 and 5 ev for a series of potassium bromide crystals (see Table I) containing $F$ centers in concentrations between $2.5\times10^{15}$ cm$^{-3}$ and $2.6\times10^{17}$ cm$^{-3}$. In Fig. 6, $\eta w_0$ is shown as a function of $F$-center concentration for photon energies of 4.2 ev and 5.5 ev. At 4.2 ev,

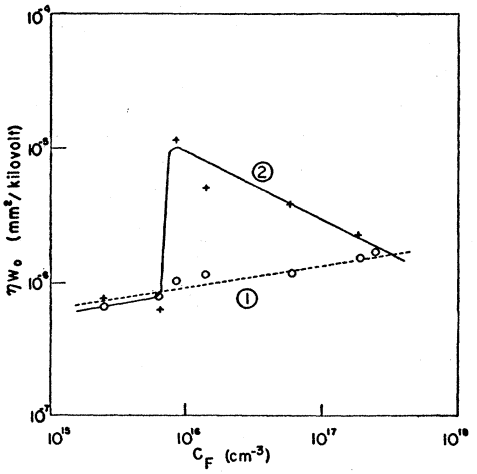

FIG. 6. $\eta w_0$ *versus* $c_F$ in KBr at 80°K. Curve 1, photon energy = 4.20 electron volts. Curve 2, photon energy = 5.50 electron volts.

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

[9] G. Glaser and W. Lehfeldt, Gött. Nachr. **2**, 109 (1936).

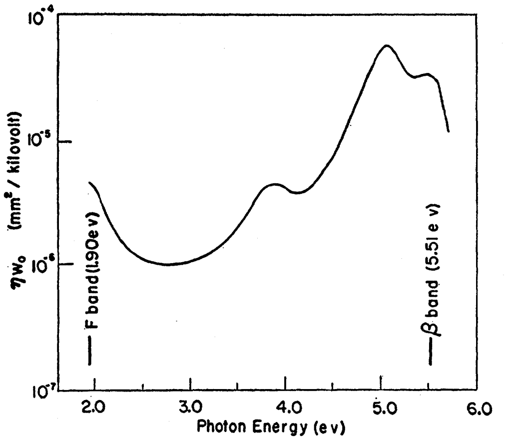

FIG. 7. $\eta w_0$ *versus* photon energy in KI at 80°K.

$\eta w_0$ is almost independent of $F$ center concentration. Since $w_0$ is inversely proportional to $F$ center concentration, the quantum yield, $\eta$ is approximately proportional to $F$-center concentration. This result suggests that these photocurrents are the result of direct absorption of photons by the high-energy tail of the $F$ band, the optical transition being from the ground state of the $F$ center to the conduction band of the crystal.

At 5.5 ev and with $c_F$ greater than $10^{16}$ cm$^{-3}$, $\eta w_0$ increases with decreasing $F$ center concentration as $w_0$ does. It appears that $\eta$ is independent of $F$ center concentration which suggests that the absorption is due to the crystal ions and is independent of the $F$ centers. The simplest assumption is that excitons are formed which diffuse through the crystal and, on collision with $F$ centers, ionize them.

Actually, the dependence of $\eta w_0$ upon $c_F$ is not quite as strong as the dependence of $w_0$ upon $c_F$, as shown in Fig. 3. The tail of the fundamental absorption band is sensitive to the mechanical and thermal history of the crystal and the optical absorption coefficient at 5.5 ev is slightly greater in crystals containing $F$ centers than it is in pure crystals. It may be that a small increase in the absorption coefficient at 5.5 ev with increasing $F$-center concentration is the explanation of the slight difference between the dependence of $\eta_a w_0$ upon $c_F$ in Fig. 3 and the data of curve 2, Fig. 6, for $c_F$ greater than $10^{16}$ cm$^{-3}$. This same explanation may also account for the fact that at 4.2 ev, $\eta w_0$ is not completely independent of $F$-center concentration but increases by a factor of 2 with the increase in $F$-center concentration from $2.5\times10^{15}$ to $2.6\times10^{17}$ cm$^{-3}$.

For $F$ center concentrations smaller than $10^{16}$ cm$^{-3}$, the exciton-induced photocurrent at 5.5 ev disappears and what appears to be the photocurrent due to direct ionization of $F$ centers remains.

This abrupt disappearance of the exciton induced photocurrent is quite mysterious. An exciton has a finite lifetime so that for sufficiently small concentrations of $F$ centers, the probability of collision of an exciton with an $F$ center decreases with decreasing concentration of $F$ centers. In the range of $F$-center concentration where the finite lifetime of the exciton is important the quantum yield, $\eta$, is expected to be proportional to $c_F$ so that $\eta w_0$ is independent of $c_F$ when $w_0$ is inversely proportional to $c_F$. Even if $w_0$ becomes independent of $c_F$ because the photoelectrons are trapped by centers other than $F$ centers, $\eta w_0$ is proportional to $c_F$.

It may be that the abrupt disappearance of the exciton induced photocurrent for $F$-center concentrations smaller than $10^{16}$ cm$^{-3}$ results from a close spatial association of these $F$ centers with impurities or imperfections. On interaction with an exciton, the effect of the impurity or imperfection is to convert the exciton energy into heat or radiation and prevent the ionization of the associated $F$ center.

## POTASSIUM IODIDE

The spectral distribution of the photocurrent in potassium iodide containing $F$ centers is shown in Fig. 7. The $F$ center concentration was approximately $2\times10^{15}$ cm$^{-3}$. The maximum of the $F$ band absorption is located at 1.90 ev and the increase in $\eta w_0$ near 2.0 ev is due to absorption of photons by the $F$ band. Maxima in $\eta w_0$ occur near 4.0 and 5.0 ev and there is a small maximum which coincides with the maximum of the $\beta$-absorption band[10] at 5.51 ev. The first fundamental absorption band has its maximum located at 5.81 ev. Measurable absorption due to the long wavelength tail of the first fundamental absorption band can be detected in these crystals at photon energies as small as 4.0 ev. A typical optical absorption curve for a "pure" potassium iodide is shown in Fig. 8. Figure 9 shows spectral distribution curves for $\eta w_0$ for four different concentrations of $F$ centers. In these experiments with potassium iodide, the concentration of $F$ centers in crystals

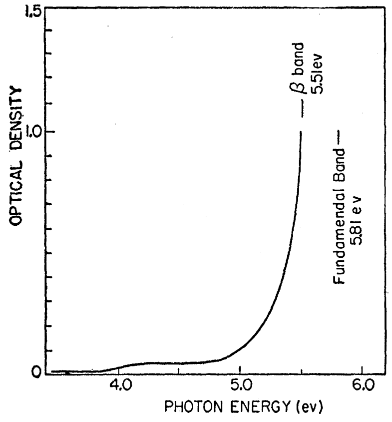

FIG. 8. Optical absorption of "pure" KI at 80°K.

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[10] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951); **20**, 746 (1952).

containing of the order of $10^{15}$ cm$^{-3}$ $F$ centers was not determined with the same precision as in the experiments with potassium bromide nor was the inverse proportionality of $w_0$ and $c_F$ checked.

If it is assumed that $w_0$ is inversely proportional to $c_F$ as in potassium chloride and bromide, it is clear that $\eta$ is independent of $c_F$ when $c_F$ is large and the photon energy is between 4.0 and 5.0 ev. In this spectral range, $\eta w_0$ decreases abruptly when the $F$ center concentration is reduced below $10^{15}$ cm$^{-3}$. The behavior is similar to that observed in potassium bromide with photon energies near 5.5 ev.

The maximum in $\eta w_0$ that appears at 5.5 ev is due to absorption of photons by the $\beta$ band. Since the height of the $\beta$ band is proportional to the concentration of $F$ centers, the maximum in $\eta w_0$ at 5.5 ev becomes less prominent as the $F$-center concentration decreases. In the crystal containing $2\times10^{17}$ cm$^{-3}$ $F$ centers, the absorption at the peak of the $\beta$ band is about 90 cm$^{-1}$ while the absorption constant of the fundamental band at the same photon energy is about 20 cm$^{-1}$. Approximately 100% of the incident radiation (neglecting reflection) is absorbed by this crystal and approximately 80% of the absorbed photons is captured by $\beta$ centers. In the crystal containing $1\times10^{16}$ cm$^{-3}$ $F$ centers, the peak absorption constant of the $\beta$ band is 5 cm$^{-1}$ and only 16% of the absorbed photons are captured by $\beta$ centers.

For photon energies greater than 5.5 ev, $\eta w_0$ decreases. This decrease in $\eta w_0$ is correlated with the rapidly increasing absorption constant of the first fundamental band whose maximum is located at 5.8 ev. The decrease in $\eta w_0$ cannot be due solely to the increasing reflectivity of the crystal which is of the order of 25% at 5.8 ev. In Taft and Apker's experiments the *photoemissive yield* behaved quite differently; the maximum yield coincided with the peak of the first fundamental band.

The experiments with potassium iodide demonstrate the existence of the same exciton induced photocurrents which were observed in potassium bromide. The photocurrent observed on excitation of the $\beta$ centers is not surprising in view of the belief that the $\beta$ absorption band is the result of the formation of an exciton by a photon which is absorbed in the immediate neighborhood of an $F$ center.[11] The small value of $\eta w_0$ for a photon energy coinciding with the peak of the first fundamental band is not understood but may be due to an abnormally small value of $w_0$ for electrons in the surface layer of the crystal. Experiments with other crystals have shown a decrease in the photoconductive yield in the spectral region where the optical absorption constant becomes very large.[12]

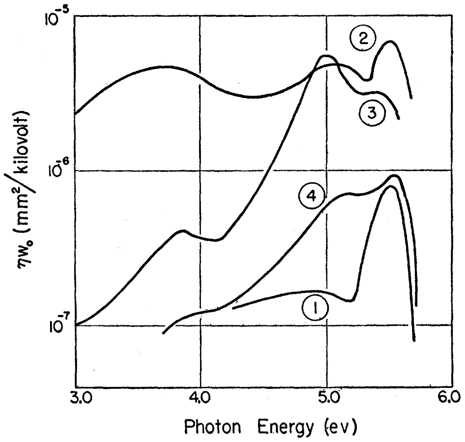

FIG. 9. $\eta w_0$ *versus* photon energy in KI at 80°K. Curve 1, $c_F=2\times10^{17}$ cm$^{-3}$. Curve 2, $c_F=1\times10^{16}$ cm$^{-3}$. Curve 3, $c_F>10^{15}$ cm$^{-3}$. Curve 4, $c_F\simeq10^{15}$ cm$^{-3}$.

## ACKNOWLEDGMENTS

The author wishes to express his indebtedness to Dr. Kenneth Teegarden and Dr. Bland Houston for assistance and his warm appreciation of the encouragement and advice of Professor Frederick Seitz and Professor Robert Maurer.

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[11] F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

[12] T. S. Moss, *Photoconductivity* (Academic Press, Inc., New York, 1952), p. 44.