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Photoelectric Effects in Certain of the Alkali Halides in the Vacuum Ultraviolet*

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An extensive search for internal photoconductivity in NaCl, KCl, KI, and LiF resulting from stimulation by light of wavelength lying below the fundamental absorption edges of these crystals has yielded negative results. Photon energies employed ranged from about 6 ev to 21 ev. Calculations based on observed external photoelectric emission currents indicate that photoelectric quantum efficiencies as low as 10^{-8} electron per incident photon could have been detected if electrons traveled completely through the crystal.

Measurements of the quantum efficiencies for external photoelectric emission by some of these crystals support the conclusion of Phillip and Taft that the valence bands of CsI and KI lie about 6.0 and 7.2 ev below the vacuum potential, respectively, and indicate that the valence bands of NaCl and KCl are 8.3 ± 0.1 ev below the vacuum. The valence band in LiF is tentatively placed at about 13 ev below the vacuum level.

Energy distribution curves for the photoelectrons ejected from NaCl and KCl by photons of energies of from 10 to 21 ev show behavior similar to that reported for Cs_3Sb, indicating that photoelectrons which have insufficient kinetic energy in the crystal to ionize another electron from the valence band will lose relatively little energy in escaping.

INTRODUCTION

THE alkali halides in pure crystalline form provide prototypes for one of the simplest types of solid compound, i.e., a cubic lattice made up of strongly ionic atoms. Theoretical investigations of the electronic structure of these solids yield best results when a tight-binding approximation is used.

It remains true, however, that, according to the general theory of the electronic structure of solids, there should exist allowed energy bands for electrons which permit the alkali halides to be electrically conducting. Results of theoretical calculations on NaCl, KCl, and LiF indicate that the conduction bands of all three should lie at about 10 ev above their respective filled valence bands, the gap being perhaps somewhat higher in LiF.[1] The bottom of the conduction band is generally presumed to be a few tenths of an ev below the vacuum level.[2]

The present work consists of an intensive search for internal photoconductivity due to stimulation by light of energy lying in the first few fundamental absorption bands of NaCl, KCl, KBr, KI, and LiF, and of investigations of the external photoelectric emission yields of NaCl, KCl, CsI, KI, and LiF. The results of the photoconductivity measurements on all these crystals are definite in showing no appreciable conductivity.

APPARATUS

All the measurements reported here were made in vacuum, the crystals being irradiated with light from a grating monochromator. The discharge lamp and monochromator were those used in earlier work.[3] The resolution of the instrument was about 5 A, disregarding the scattered light from the grating, which light was of major importance in the photoelectric measurements. The lamp, monochromator, and detector head were separately pumped, being separated by baffles so that the residual gas pressure in the detector head was 10^{-4} mm Hg or less. During the operation of the lamp, the hydrogen pressure rose to about 10^{-3} mm Hg in the detector chamber. The fact that this pressure was unimportant in the measurements was determined by sealing off the entrance slit to the monochromator with a LiF filter and using a liquid nitrogen trap in the detector head, thereby reducing the total pressure in the detector head to about 5×10^{-6} mm Hg.

Using data from Brode,[4] it was decided that at any of the prevailing hydrogen pressures, the photoelectron energy losses to the gas should be negligible. The results of tests made at both the high and low hydrogen pressures confirmed this, since they were identical within the experimental errors. Because it was desired to make retarding potential measurements at photon energies to which LiF is opaque, no windows were used in the final measurements and the presence of the relatively large hydrogen pressures was hence accepted. Whether the presence of such hydrogen had deleterious effects on the crystals is another and open question.

The intensity of the incident radiation was monitored by means of a sodium salicylate transmission phosphor which was sprayed directly over the photocathode of an RCA 5819 photomultiplier tube. This phosphor has been studied and found to have a constant quantum efficiency at least between 900 A and 2000 A.[5] The photomultiplier was mounted directly in the path of the light beam by means of an O-ring seal through the end cover of the detector chamber. The photomultiplier output was connected through a 100-kilohm Ayrton shunt to a galvanometer whose sensitivity was 5×10^{-10} amp/mm and whose time constant was 2 seconds. The photomultiplier dark current was about 10^{-9} amp and the signals ranged

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† Now located at the Los Alamos Scientific Laboratories. Work done in partial fulfillment of the requirements for the Ph.D. degree.

[1] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 407-56.

[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1940), p. 97.

[3] Hartman, Nelson, and Siegfried, Phys. Rev. **105**, 123 (1957).

[4] R. B. Brode, Revs. Modern Phys. **5**, 257 (1933).

[5] K. Watanabe and C. Y. Inn, J. Opt. Soc. Am. **43**, 32 (1953).

from 10^{-8} to 10^{-6} amp. The galvanometer readings were stable to within better than 1% during any given measurement.

Measurements of the external photoemission currents for the spectral yield curves for crystals were made with a Victoreen VX-41A electrometer tetrode connected as a current amplifier with 10^{10}- and 10^{11}-ohm grid resistors which could be used alternatively. The electrometer tube and the associated circuitry were mounted on Lucite insulation in vacuum within the detector head. This arrangement kept the grid capacitance to a minimum and precluded the possibility that the high-impedance insulation would become dirty or contaminated by moisture from the atmosphere. Such an arrangement also serves to shield the sensitive lead from changing electric fields in the laboratory and to keep the electrometer tube in darkness, thus eliminating photoelectric emission from the electrometer tube grid, which can result in a spurious signal.

The output of the electrometer tube was connected to the galvanometer through the Ayrton shunt, to which was added a second set of resistors on a gang switch in order to keep the resistive plate load on the electrometer constant at 100 kilohms. The maximum current gain of the circuit was 2×10^5 or 2×10^4, depending on which of the two grid resistors was used, and it was found that currents as small as 5×10^{-14} amp could be detected reproducibly. The drift rate of the output circuit was not greater than 2×10^{-8} amp per hour after a short warm up period.

This circuit was also used for a few of the measurements in which attempts were made to detect internal photoconductivity. Most of these measurements, however, and all of the retarding potential measurements of external photoelectrons, were made with an Applied Physics Corporation vibrating reed electrometer. This instrument was supplied with a range of input resistors to 10^{12} ohms, making it possible to detect steady currents as small as 10^{-16} amp, so that the practical lower limit of detection was about 2×10^{-16} amp. For such measurements, it was necessary to bring the current lead through a high impedance shielded connection out of the vacuum to the electrometer input. Ordinary glass seals are notably inadequate. A useful and simple solution to this problem was obtained with a demountable seal made up around a short tube of Vycor glass. This is sketched in the insert with Fig. 1. The sensitive lead is in two parts which thread together within the Vycor tube, compressing a $\frac{1}{8}$-in. diameter O-ring between themselves and the inside wall of the Vycor tube, the ends of the conductor then protruding somewhat from the tube. This small unit is then passed in an external compression O-ring seal around the outside of the Vycor through the metal vacuum wall. This seal has been very satisfactory, having a resistance of better than 10^{15} ohms and being quite insensitive to humidity. Cleaning in alcohol is easy in case of careless handling.

A general schematic diagram of the detector head is shown in Fig. 1. The adjustable defining exit slit (5) for the light beam is mounted in a separate end plate (15) on which was built up the supporting mount (4) for the electrometer tube (2) and associated circuitry, and for the electrode systems used for the various measurements. It was possible to move in or out of the light beam through a sliding seal various filters (6) to make some degree of correction for scattered light.

The apparatus used for measuring spectral yield curves consisted of a cylindrical brass collector electrode (7) (referred to hereafter in the photoelectric measurements as the external collector). This assembly and an attached mounting (10) for the crystals (11) and thin films was attached to the monochromator exit slit tube by means of $\frac{1}{8}$-in. diameter quartz rods (14). The collector electrode was 1 in. in diameter and $1\frac{1}{2}$ in. long. It was closed at both ends and was milled off on the side nearest the monochromator. To the milled-off region was mounted a separate brass electrode (9) which was insulated from the main cylinder by Lucite spacers (8). This separate electrode would thus be maintained at any desired potential relative to the cylindrical collector. The purpose of the second electrode was to collect any photoelectrons from the exit slit of the monochromator if this were found to be necessary.

Single crystals and thin films were mounted just in

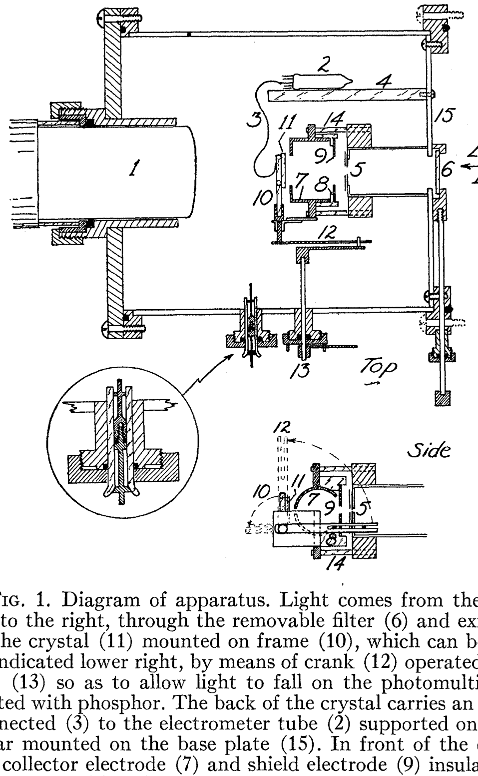

FIG. 1. Diagram of apparatus. Light comes from the grating, far to the right, through the removable filter (6) and exit slit (5) to the crystal (11) mounted on frame (10), which can be flipped, as indicated lower right, by means of crank (12) operated through seal (13) so as to allow light to fall on the photomultiplier (1) coated with phosphor. The back of the crystal carries an electrode connected (3) to the electrometer tube (2) supported on a Lucite pillar mounted on the base plate (15). In front of the crystal is the collector electrode (7) and shield electrode (9) insulated from it by Lucite (8), this assembly being supported from the exit slit by quartz rods (14). The insert at the lower left indicates the construction of the high impedance demountable seal used when the vibrating reed electrometer was employed rather than the internal electrometer tube. It is self explanatory.

front of the exit slot in the collector electrode on frames bent up out of quartz rod. These could be flipped back by the crank (12) rotated through an O-ring seal (13) so that the samples could be removed from the light beam, thus allowing the light intensity to be monitored by the phototube (1).

Retarding potential measurements were made by installing, as seen in Fig. 2, a separate base brass plate (11) and monochromator exit slit (5) assembly in the detector head. On this plate was mounted by the support (8) (9) a spherical collector (6), which consisted of a 3-in. diameter chemical flask coated internally with graphite, to which the electormeter lead was connected by means of a nickel contact spring (3). The resistance between the sensitive leads and any attainable point on the graphite was not much more than 10 kilohms, which assured that there was no significant potential gradient through the graphite.

Samples to be studied were evaporated on a nickel plate (1) which was inserted into the sphere through the neck of the chemical flask, and which could be rotated by means of an O-ring seal (13) (10) through the vacuum wall. In this way the reflected light beam from the sample could be passed out through a hole (4) in the sphere, 90° displaced from the entrance hole. This procedure eliminated the necessity of making corrections to the data for reverse photoemission from the collector sphere when large retarding potentials were used. Directly behind the nickel substrate and attached to the same movable mounting was a nichrome heater wire (2), which was used for annealing the films. In order to monitor the temperature of the films, a chromel-alumel thermocouple was spot welded to the back surface of the nickel. The detector chamber was pumped through (12) (not seen in Fig. 1).

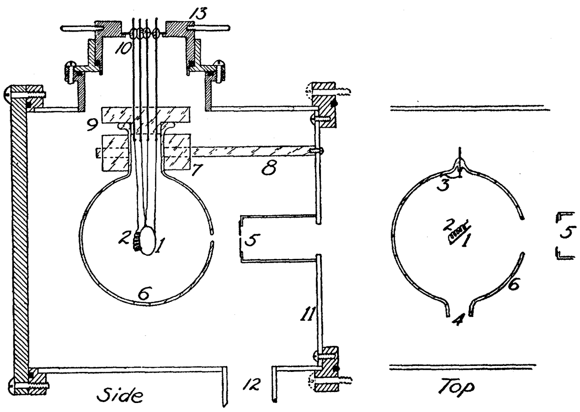

FIG. 2. Diagram of apparatus used on photoemission retarding potential measurements. Light comes, as in Fig. 1, through a removable filter and exit slit (5) to the emitter evaporated externally on the electrode (1), heatable with heater (2). These are carried on a crude Lucite bearing (9) and rods sealed (10) into a head (13), rotatable to reflect light out hole (4) in the spherical collector (6) connected through (3) to the electrometer as shown at the right. The sphere is supported rigidly by clamp (7) and rods (8) to base plate (11). Pumping is through port (12).

Some measurements were made at wavelengths below 900 A. These necessitated the use of a helium discharge in the lamp. The precision of these measurements was not as good as that of measurements made with the hydrogen discharge, principally because the intensity of the helium lines varied fairly rapidly in consequence of the poor gas leak used to admit the helium to the lamp.

SCATTERED LIGHT

It cannot be overemphasized that discussion concerning the magnitude of scatttered light from any monochromator is not too meaningful without clearly specifying what the detector is, unless, of course, one has the spectral distribution of this light. The radiation from the hydrogen lamp, and hence passing through the monochromator entrance slit, ranges in wavelength from the far ultraviolet to the infrared. The photomultiplier, sensitized with a semitransparent phosphor on its face, is sensitive to all wavelengths between the short-wave ultraviolet and approximately 6000 A. Its response to the total scattered light coming through at the particular monochromator setting will represent one measure of the scattered light. Other detectors, such as an alkali halide photoemitter, to be discussed, are sensitive over an entirely different region of the spectrum and accordingly "see" entirely different scattered light intensities.

The long-wavelength limit of the ionization continuum of the hydrogen source was taken to be at about 800 A. It was therefore assumed that for all monochromator wavelength settings less than this, the entire beam incident on the exit slit was scattered light. This assumption is not absolutely correct, but when one used the photomultiplier and phosphor as detector, the error is not more than a few percent at most. Actually, a few lines (probably due to impurities) were found down to nearly 300 A, but their intensities as determined by this detector were not more than 3% of the total reading. The true scattered light intensity rises continuously and smoothly as the monochromator is turned to shorter wavelength settings. The true and weak very-short-wavelength lines are much more easily detected by the photoelectron emission which they cause from LiF, since the LiF is relatively insensitive to the scattered light of longer wavelength.

The undesired light arises both from the fact that the second order diffraction spectrum is nearly $\frac{1}{3}$ as strong as the first order with the grating used, and from the fact that there is some general true scattering by the grating, seemingly rather more than is given by modern rulings. The second order light is not very important when the monochromator is set for wavelengths shorter than about 1700 A, but for all longer wavelengths, it becomes necessary to use filters in the beam. For wavelengths less than 1700 A, the unwanted light seen by the photomultiplier is mostly due to scattering and increases monotonically toward the shorter wavelengths. At wavelengths greater than 1000 A, one can usually set the monochromator on a line for which the intensity is sufficient, so that the scattered light is only a small percentage of the total light seen by the photomultiplier.

The great difficulty arises from the fact that the photoelectric yield of the alkali halides changes by about 10^3 over about 100 A range near the emission edge, and consequently the positions and shapes of the edges are obscured by short wavelength ultraviolet scattered light. For example, with the lamp and monochromator used in this work, at 1400 A the photoelectric signal-to-background ratio for KCl is one-to-one.

Such error introduced by scattered light can be minimized in two ways: the short-wavelength scattered light can be greatly reduced by means of filters cutting off below the wavelength being used, or the contributions of the scattered light must in some way be subtracted both from the photoemission currents and the light-intensity measurements. Both of these techniques were employed, and, within the accuracy of either, they gave the same results for the shape and position of the photoelectric emission edge for NaCl and KCl. The filters used were of CaF_2, which has a short-wavelength cutoff at about 1250 A, so eliminating the strong lines of the Lyman series.

The subtraction method was made as follows: for the intensity corrections, photomultiplier current readings were taken at wavelength settings of between 0 and 800 A, for which the output was taken as being caused only by scattered light. A log-log plot of this scattered light intensity *vs* wavelength setting yielded a straight-line plot which was extrapolated into the interesting and useful wavelength region to give the scattered light correction over the range of wavelength settings of useful light output. The validity of the extrapolation was checked by putting LiF, CaF_2, NaCl, synthetic sapphire, and glass filters in the beam and making similar output measurements and plots. These were made over a range of wavelength settings less than the corresponding filter cutoff, which are, respectively, 1050 A, 1250 A, 1450 A, 1750 A and, for the glass, probably around 3500 A. The plots so obtained were found to be nearly parallel to each other and to the curve taken with the unfiltered beam.

Since the intensity of the lamp varied from day to day, these curves could not be used directly without some sort of normalization for lamp intensity. It was possible, however, to do this simply by shifting the curve to a parallel line, the amount of the shift being determined by taking one normalizing datum point, say, at a wavelength setting of 600 A.

To correct photoemission currents for the contribution from scattered light and because the spectral distribution of the scattered light was apparently not the same at different wavelength settings of the monochromator, a pseudo quantum efficiency for the crystal in response to the scattered light was determined at wavelength settings below 800 A. For wavelengths longer than that at the threshold there was no change in the observed photoemission between adjacent maxima and minima of the hydrogen spectrum, so all emissions in this region were likewise ascribed to scattered light. Pseudo quantum efficiencies were therefore calculated for these points and a smooth curve drawn through and connecting the short-wavelength and long-wavelength sets of points. Such curves, together with the above-decribed scattered light intensity plots, both normalized for lamp intensity variation, were used to correct data in the intermediate and useful region of the spectrum. This procedure was followed for the work on KCl and NaCl.

The data on KI and CsI were taken with sapphire and NaCl filters in the beam, and no subtractive corrections needed to be made. Nor did the data on LiF require subtractive correction. As will be seen, up to and in the vicinity of its poorly defined threshold, taken to be at 12.5 ev where the second and sharp rise in the external yield occurs (an energy high enough that there is but little scattered radiation of higher energy), LiF has only a low yield. Furthermore, high-intensity lines are available for use on the low-energy side of the threshold, making intensity correction unnecessary. At energies higher than the threshold, however, it did become advisable to correct the light intensity as measured by the photomultiplier and phosphor detector. Correction to the external LiF photocurrent was still nevertheless trivial in this region.

Photoelectric retarding potential measurements made at photon energies of 10.2, 12.1, and 21.2 ev, discussed later, required no scattered light corrections because the spectral lines at these energies are relatively intense. Retarding potential measurements made, however, at 13.8 ev required correction for scattered light by methods similar to that outlined above.

PHOTOCONDUCTIVITY MEASUREMENTS

In this work, many attempts have been made to detect intrinsic photoconductivity, resulting from the direct transitions from the valence band to the conduction band in NaCl, KCl, KI, and LiF, principally the first two. The experiments were done on optical-quality single crystals obtained from the Harshaw Chemical Company, and on evaporated films made from powders ground from Harshaw crystals. Some experiments were also tried on KCl and NaCl single crystals obtained from Korth, in Germany.

One great difficulty encountered in any attempt to measure photoconductivity in pure alkali halide crystals in the region of their fundamental optical absorption bands is that the extinction coefficients for light in these regions of the spectrum are between 10^5 and 10^6 cm^{-1}, so that the density of free electrons and holes created by the absorption of the light is appreciable only in a very thin layer near the surface. Thus one might expect a very high recombination rate and to observe, at best, photocurrents which would perhaps not be proportional to the light intensity. At the worst, it might result that the recombination rate is so high, or that impurity or

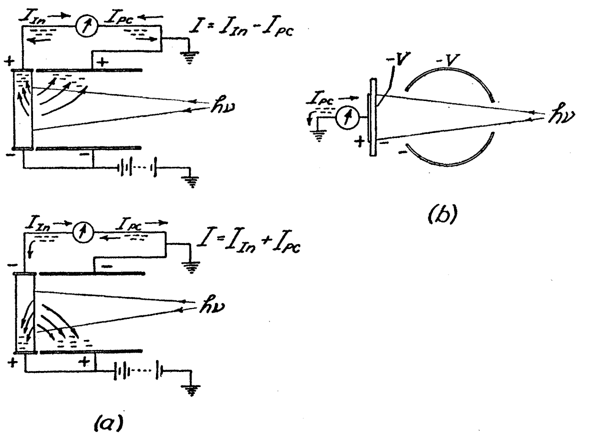

FIG. 3. Diagram indicating method of measurement of transverse photoconductivity (a) and that longitudinally (b). The direction of motion of negative charge arising from induced effects in the external circuit and any direct internal electron motion are indicated.

dislocation traps near the surface are so dense, or that the surface properties are so different from the volume properties of the bulk crystal, that no photoconductivity can be observed.

Unpublished attempts to measure photoconductivity and photoemission in NaCl were made a few years ago in this laboratory. Silver electrodes were painted on opposite thin edges of cleaved single crystals. External collector electrodes in the same plane with these edges were fixed in front of the broad face of the crystal as indicated in Fig. 3(a). It was the purpose of these electrodes to aid in establishing a field across the crystal and to collect the external photoemission electrons. The crystal was mounted on a Lucite holder so that it could be removed from the beam in order to measure the intensity of the beam, which irradiated the central region of the crystal.

The measurements were made as follows: With the electrometer grid connected to the electrode on one edge of the crystal and to ground through the grid resistor, and with the adjacent external electrode shorted to ground, Fig. 3(a), the opposite electrodes were put at the same potential of +1400 volts. While potential distribution measurements were never made, it was assumed that a field was thus eventually set up, more or less uniformly, over the whole of the crystal. A $\frac{1}{6}$-second light flash was allowed to fall on the crystal resulting in a net ballistic signal current, I. External photoemission (or any internal electron motion away from the irradiated region) would leave a positive charge on the crystal surface, which, by induction, shows up as a current pulse I_{In}, adding to any photoconductivity pulse I_{pc}. Then with the high-voltage electrodes negative, at -1400 volts, the induced-current signal from the photoemission is still in the same direction but the conductivity pulse is reversed. Thus, in the first instance $I_1 = I_{\text{pc}} + I_{\text{In}}$, and in the second case $I_2 = I_{\text{In}} - I_{\text{pc}}$, the two relations allowing both unknowns to be determined. The actual external photoemission current was to be measured by connecting the electrometer grid to the external electrode and performing a similar pair of measurements. In fact, any photoconductivity current I_{pc} would also probably show as an induced signal only, since it is extremely unlikely that any direct electron flow reaches the electrometer electrode from the irradiated region.

After each such measurement, an attempt was made to discharge the crystal by reducing the voltage applied across it back to zero and then spraying the surface with electrons emitted from a heated tungsten filament held at ground potential. Upon then reapplying the voltage to the crystal, one naively hoped that the original potential distribution was re-established, or at least closely approached. In fact, however, it was never possible to obtain results which were sufficiently consistent to be regarded as reliable, either the induced effects from photoemission over-riding the effects of internal charge motion, or variations in the potential to which the crystal is returned leading to variations in the charge subsequently removed in irradiation.

One of the great difficulties in any such measurements on insulators is the effect of polarization and depolarization of the material. If the potential of a floating surface of a crystal is suddenly changed, say to that of an external source supplying electrons which can reach the surface, there is a corresponding transient change in the potential of an electrode capacitively coupled to it, if the electrode is grounded only through a high resistance. This is the case in measurements here, where an electrometer is driven by the voltage appearing across the resistance. Following this, small internal currents may continue to flow, lowering the surface potential with time in a way not directly measureable. This therefore allows the possibility that the surface is at a potential not intended when subsequently irradiated with light. At the same time it might appear, as it did here, that such internal currents would also appear in the electrometer. But this is not necessarily so.[6] If one takes, for example, a crystal with its front surface floating but negatively charged, and releases electrons at the surface into the conduction band by light absorption, it is all too likely that no current will be seen by the back and electrometer electrode, connected to ground through a high resistance. Only if the front-surface capacitance to external fixed potential electrodes is comparable with that to the back electrode, will something be indicated. The more familiar situation is that of an isolated and charged two-plate condenser with one plate floating in potential and the other connected to ground through a galvanometer. The galvanometer will indicate no change as the floating plate is moved toward the fixed plate. The field and hence the charge at its surface remains fixed. All the lines of force from the charge on the float-

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[6] We are indebted to Dr. A. Rose for kindly pointing this out to us in a comparison with similar measurements made at the RCA Laboratories on zinc-oxide coated "Electro-fax" paper.

ing plate end on the fixed plate regardless of their relative positions. While all such effects should not be so manifest in the case of a crystal clamped between two electrodes held at a fixed potential difference (save for transients), there is every likelihood even here that at least the potential distribution between them comes to something different than linear as would be desired.

There was also concern in these early transverse conductivity measurements that the magnitude of the electric fields obtainable by this method might not be great enough to give appreciable electron displacement in the crystal and, furthermore, that any possible conductivity observed might be more indicative of the surface state than of the volume state of the crystal. While there was also concern over possible tungsten evaporation from the discharge filament onto the surface of the crystal, this could in principle be avoided by operating the filament at low temperatures, the vapor pressure of the tungsten falling much more rapidly than the emission.

It was, in any case, decided that more unambiguous results could best be obtained if the photoconduction electrons were drawn into the crystal longitudinally with the light beam, as in Fig. 3(b), which would allow the external photoemission to be minimized and, where present, to always subtract from the desired signal to be observed (except where there is photoemission from external electrodes to the crystal surface). By this method it would also be possible to obtain higher electric fields across the crystals, which could now be made very thin. To avoid possible tungsten contamination, it was decided to discharge the crystal by photoelectric emission from nearby metals, the light being incidentally directed onto the metals by reflection from the crystal or by merely making sure that a portion of the incident beam touched a grounded metal surface. The apparatus used has already been described.

Crystals of NaCl, KCl, and KI were cleaved to approximately 10×10×0.5 mm (worked on under an infrared heat lamp to inhibit deliquescence) and (while still warm) were mounted in the vacuum chamber with Duco cement onto the quartz frame mounts. An electrode (and fine connecting wire) silver-painted to the back surface was held at ground potential through the electrometer while the front surface of the crystal was brought to some large negative potential before each measurement. Measurements were made by one of four methods.

(1) After allowing a long time for the crystal to depolarize in the absence of any applied fields or stimulation by radiation, the cylindrical collector electrode used for photoelectric emission measurements was connected to a high-voltage power supply and the potential was gradually lowered to -1500 volts. The electrostatic potential between the external electrode and the grounded back electrode on the crystal was relied on to polarize and establish an electric field across the crystal such that electrons could then move into it toward the back surface. The separate electrode mounted contiguously with the external collector and insulated from it by Lucite was set at a small positive potential so that photoelectrons created by reflected light falling on it could not travel to the front surface of the crystal. However, in spite of the intervening negative-potential region, electrons were able to reach it from the crystal, such that only a transient photoemission from the crystal surface was detected. Because of this the separate electrode was connected electrically to the cylindrical collector, and the angle of the crystal carefully adjusted so that the reflected beam from the crystal passed back through the slot in the collector electrode without touching the metal. With this arrangement, no current was observed when light was incident on the crystal. The desired current was sought for ballistically in this method.

(2) The front surface of the crystal was charged to near the potential of the external electrode by photoemission from a small piece of tantalum sheet which was kept at the same negative potential as the external electrode. A mercury light source was used to stimulate this emission and at the same time the vacuum ultraviolet light was allowed to fall on the crystal. It had also been hoped that if the previous negative results had been the result of trapping of electrons to create F centers, the mercury light would continually empty the traps and lead to a steady state current. Actually, with the mercury light alone, electron current flow to the back electrode was indicated. This would decay only somewhat and then seemingly continue indefinitely, possibly from an electron flow through vacuum from an unintended photosource. Upon then irradiating the crystal with the vacuum ultraviolet light, one then got only a transient indication of the usual sign caused by the photoemission from the crystal surface to the external collector.

(3) A nickel screen of three-mil wire and approximately six-mil spacing was laid directly on the front surface of the crystal and held at negative potentials as large as -1000 volts. It was found, however, that the crystals here exhibited photoelectric emission to or from the external collector electrode, depending on its potential, indicating that the areas of the crystal between the wires of the screen were not maintained at the potential of the screen nor shielded by it, even though they were charged by photoemission from the screen. While no positive result was observed here, it has since seemed that some possibilities of this arrangement or variations on it were overlooked and that it might well be tried again in future work contemplated.

(4) Onto the front surface of the crystal a thin film of gold was evaporated, to one corner of which was attached by silver paint a three-mil copper wire maintained at the desired potential, The thickness of the gold film was controlled by previously attaching a three-mil wire to each of two opposite corners of a test sample crystal and evaporating gold onto it until the electrical resistance between the two wires, measured with an ordinary ohmmeter, was approximately 1000 ohms. Immediately adjacent to this crystal in the evaporator was

a thin LiF crystal also taking on a similar gold film. Care was taken to assure that the two crystals were arranged symmetrically with respect to the evaporation filament so that it could be then assumed that the thicknesses of the two gold films were equal. The transmission of the gold film in the vacuum ultraviolet was then measured by using this gold-evaporated LiF crystal as a filter in the vacuum monochromator. It was found that the 1215 A line could still be distinguished through a gold film on LiF if the duplicate film on the crystal to be studied had a corner-to-corner resistance of as low as 160 ohms. At a resistance of 1000 ohms, the films still had on the order of 50% transmission. In the photoelectric measurements made on both NaCl and KCl crystals having such transparent front electrodes, no photoconductivity was observed.

The greatest problem with these front-evaporated films is that even if the corner-to-corner resistance is made low, there may be areas on the surface which are well insulated from the high-voltage lead, such that upon irradiation with ultraviolet light, photoelectric emission to or from these areas results in potential changes of these areas. The resulting induced signal at the back-surface electrode is easily mistaken for photoconductivity. In order to guard against such spurious results, a sample was rejected unless it met the following test: the connection to the thin front-surface electrode was shorted directly to ground, and the external collector electrode was made 45 volts positive with respect to it. If the gold film on the front surface of the crystal was electrically continuous, no effect was observed on the electrometer connected to the back surface electrode when the ultraviolet beam was allowed to fall on the front surface, even though there was a large photoemission current from the front gold electrode.

The assumption that it might be possible to detect fairly large ballistic signals with these techniques was based principally on the alpha-particle work of Witt.[7] As in his work, some of the measurements in the present experiments were made at field strengths on the order of 10^5 volts/cm; yet even in cases where light from the central image of the illuminated entrance slit was incident on the crystal, which illumination is many times as strong as even that of the bright 1215 A Lyman alpha line, no photoconduction effect was observed. This is certainly not to be expected, for the penetration depth of alpha particles and ultraviolet light are of the same order of magnitude. However, the electrons released by alpha-particle bombardment are of much higher energy than those released by 10- or 20-ev photons. Actually, some measurements were made at photon energies of the latter value, when a helium discharge, substituted in the lamp for hydrogen, made possible the use of the 21.2-ev line at 585 A.

From time to time in the measurements on these crystals with the transparent front electrode, the latter was allowed to float in potential and a check was made to insure that the large photoemission current from the electrode would produce the expected drastic effect on the electrometer indication. Most of the measurements were made with the crystals in the dark (save for the ultraviolet irradiation) but others were made with strong mercury radiation falling on the crystals through a quartz window from the outside. KCl, NaCl, KI, and LiF were studied using this transparent electrode.

In LiF, small photoconductivity currents were observed when the incident light was in the wavelength range from 1200 A to 1050 A, but light at shorter wavelengths, where the absorption of LiF is high, produced no measureable results. These currents behaved with illumination and field as one expects of photoconduction currents and are believed to be such. Since it is not believed that this conductivity is associated with the fundamental absorption, it was not studied in detail in this work. It is felt that the effect may be connected with the long-wavelength tail observed in the LiF photoemission to be discussed later. This current is presently being pursued further. It may be of considerable significance to the other negative results, that this conductivity disappeared when the absorption went to high values.

Similar experiments to the above were carried out on very thin single crystals. For these experiments, crystals 10×10×1 mm were milled out on one side with a dental burr over a central rectangular region until they were about 0.010 in. thick, leaving a thick supporting rim around the outside. These central regions were then dissolved away further on the milled side with a fine brush dipped in water until they were 2 or 3 mils thick. They were then annealed for an hour at temperatures in excess of 500°C. When annealed in vacuum, the thinned region frequently disappeared. One can go to higher temepratures if the annealing is done in air but the uncertainty concerning effects of air on the hot surface is also disturbing. After annealing, these thinned crystals had thick gold electrodes evaporated on the worked back surfaces and, in some cases, thin transparent gold electrodes evaporated on the cleaved and preserved front surfaces. Such crystals were installed in the detector head of the monochromator immediately after the last evaporation in the same manner as with the thick crystals. This type of crystal was checked for photoconductivity in the manner of methods (1), (2), and (4). Negative results were obtained for NaCl, KCl, and KI, all thinned in this way.

One of these crystals, of KCl with a thin transparent front-surface electrode, exhibited a very small voltage-dependent signal, corresponding to electron emission from the front to the back surface, when it was irradiated with the 1215 A line or with the central image of the entrance slit. When filtered by a thin wafer of CaF_2, which has a short-wavelength cutoff near 1260 A, the central image had no effect on this crystal. The magnitude of the observed current could be interpreted by

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[7] H. Witt, Z. Physik **128**, 442 (1950).

assuming that photoemission electrons from the front gold electrode, or from the KCl itself, had moved about 300 A into the crystal. On the other hand, since the current was not observed to decay after times on the order of 10 minutes, it would be more plausible to assume that the electrons traversed the full distance across the crystal, but were being released with an efficiency some 10^4 times smaller than that at which external photoelectrons are released when the 1215 A line is the incident radiation. It was found that if the crystal was exposed to the 2536 A line of mercury, with sufficient intensity to produce photoemission from the gold of magnitude comparable to that produced by the 1215 A line, a continuous photoconductive effect of almost the same size was produced. The nature of this effect is still not thoroughly understood, but it probably involves a reduction of the finite dc resistance of the crystal in a rearrangement of the electric field in the crystal,[8] as well as the sort of current injected from surface electrodes into additively colored alkali halides as studied by von Hippel and his co-workers.[9–11]

One crystal each of NaCl and KI, similarly prepared to give a thin crystal, exhibited a photoelectric effect which resembled photoconductivity, except that it was completely independent of the potential of the transparent surface electrode, even as to sign. In both cases the front electrode effectively shielded the sensitive electrode from the effects of photoemission from the front surface, as it should. The signal which behaved in this manner decayed rapidly in NaCl, but remained at full value indefinitely, as long as the crystal was exposed to light, in the KI. These were certainly not in the general behavior pattern of most of the experiments. While it is not understood, whatever was happening here is considered as spurious to true photoconductivity.

Experiments were tried in which photoconductivity was looked for in thin films of NaCl and KCl. These were evaporated over a thick gold film substrate and themselves then covered with a transparent evaporated gold electrode, the whole operation being performed without removing the sample from the vacuum until after the last evaporation. The area of the substrate back electrode was considerably less than that of the overlying alkali halide film and transparent electrode, to minimize leakage current at the edges of the back electrode. The KCl and NaCl films here had thicknesses (estimated from the interference patterns produced by the films deposited on glass slides in the same evaporation) of between 10 000 and 20 000 A, and were obviously not single crystals. The films had surprisingly high ohmic resistances, that of the KCl presenting a dark resistance of about 10^{13} ohms between gold electrodes while that of the NaCl, the thinner of the two, was better than 10^{11} ohms. No effect of irradiation with ultraviolet light which was voltage-dependent was detected, although all the usual external photoemission currents were observed.

Another attempt to measure any possible surface photoconductivity in NaCl and KCl, in possible contrast to a volume effect, was made by evaporating two gold electrodes shaped like block *T*'s on the surfaces of single crystals of these salts. The two *T*'s were placed in opposition leaving a clear 2-mm strip of crystal surface between the cross *T*-members, electrical connection being made at the foot of each *T*. Over the entire surface was then evaporated a thick layer of LiF. This was intended to prevent any external photoemission, at least to the LiF emission edge, thought to be well below that of NaCl and KCl. The light beam was incident through the LiF on the 2-mm strip between the gold electrodes, but overlapped onto them. Between the electrodes a voltage of about 1500 volts was applied. All that was learned definitely from this was that the LiF has a rather long tail in its photoemission yield curve which extends well into the long-wavelength region, as will be discussed. The currents measured were not freed of photoemission effects and were simply some fraction of what would have been obtained had the entire photoemission from the LiF films been measured. For example, with the external collector electrode positive to both of the crystal electrodes, the observed currents were independent of the potential difference across the irradiated gap.

On the suggestion that an etched surface might very well be preferable to cleaved surfaces from the standpoint of charge recombination and trapping, some experiments were redone with the irradiated surface not a freshly cleaved surface but rather one water etched after cleaving. The arrangement described in the preceding paragraph was done over with such NaCl and KCl crystals as were the experiments utilizing the thin single crystals. All the results were negative. The KCl-etched and thinned down crystal showed the small voltage-independent current previously noted in the case of NaCl and KI; these currents decayed rapidly but would build back up after the light was removed for a minute or so.

In all the arrangements having gold electrodes on both the front and back of the crystal, an attempt was also made each time to detect any hole conductivity, by making the front-surface electrode positive instead of negative. The results were again negative.

In evaluating the above results, it should be noted that if the schubweg of 10^{-7} cm^2 per volt quoted by Witt,[8] and Flechsig,[12] (Harten[13] quotes 10^{-8} to 10^{-9} cm^2/volt on the basis of x-ray induced conductivity), is valid in these experiments (it may well not be, since these are uncolored crystals), a field of 10 000 volts/cm should have been sufficient to move electrons all the way through the very thin crystals tried here. Since no cur-

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[8] F. Stockman, Z. Physik **147**, 544 (1957).

[9] A. von Hippel *et al.*, Phys. Rev. **91**, 568 (1953).

[10] M. Geller, Phys. Rev. **101**, 1685 (1956).

[11] M. A. Gilleo, Phys. Rev. **91**, 534 (1953).

[12] W. Flechsig, Z. Physik **46**, 788 (1928).

[13] H. Harten, Z. Physik **126**, 619 (1949).

rent was observed at fields many times this strength (the thin crystals were used with 150 volts across them —some of those between $\frac{1}{2}$ and 1/mm were tried with voltages of up to 15 kv), one can put an upper limit on how far they actually did move, on the basis of a few experimental facts. It had been observed when photoemission data were taken, that under irradiation by the strong 1215 A line, the front surface of a single crystal charges up to a potential of 10 volts or more in about 1 second. With time, charge is building up in the surface region so reducing the field intensity immediately behind the front surface until, ultimately, no more charge is moved out of the region and any detected charge flow ceases. In this state, the front surface equipotential has been moved toward the back surface. If such a space charge accumulation caused the potential of the front surface to move toward the back electrode by as much as one part in 10^5 of the crystal thickness, or a distance of 100 A in the case of a 1-mm crystal, the effect could have been detected on the vibrating reed electrometer, which, with the 10^{11}-ohm input resistor, has a time constant of 1 second, and which is sensitive to input voltages as small as 0.0001 volt. One would surely expect the fundamental transition from valence band to conduction band to be as probable as the external ejection of an electron, so that at least with the 1215 A line, charge displacements of the above order of magnitude (and less in the thin crystals) should have been detectable. For weaker irradiating lines, the process would go slower and a larger upper limit on the displacement would have to be given in such cases. On the other hand, if charge were to move all the way through the crystals, a limit on the quantum yield can be given. We take the external photoelectron yield at 1215 A to be about 0.1 electron per photon, as will be seen to be the case, and we measure, at the high lamp output level used to stimulate photoconductivity, an external current of about 10^{-9} ampere under this strong irradiating line. (In general the source intensity was about 100 times weaker when external photoelectric measurements were being made, but at the intensities used for the photoconductivity work such external currents could be obtained.) This gives us the photon flux, which on producing an an internal current of less than 10^{-16} ampere leads to a photoconduction yield of less than about 10^{-8} electron per photon. It certainly seems more reasonable that some process rather limits the electron motion to very short distances.

Thus, the results of all these measurements would indicate that there is no observable photoconductivity induced in the alkali halides by light of wavelength in their fundamental absorption regions, at least within the limit of sensitivity of detectors used in this work. It should be recognized that these measurements were all done at room temperature, with commerically available materials, in a not extremely clean vacuum system with certainly a fairly high partial pressure of hydrogen present, and in the presence of generally copious external photoelectric emission. Nor were all of the measurements done with the most sensitive detector.

It is very difficult to believe that our picture of ionic crystals is grossly in error and that transitions from the valence band to the conduction band cannot be induced by photon irradiation. It consequently presents something of a problem to understand these results. It is true, of course, that in the alkali halides, the optical absorptions are very high and consequently the absorption involves only a thin surface layer of the crystal, generally about 100 A thick. It is quite conceivable that conditions in this layer are considerably different than in the bulk of the crystal. Trapping and recombination at the surface, the state of which is only crudely known in this work, may be so high as effectively to prevent any charge motion. This could be caused either by impurities or by dislocations. There may also exist high electric fields in this region which override any applied fields used, such that no net accelerating field is present to move electrons, except possibly out of the crystal surface. In the light of this possibility, one may hazard the suggestion that the sharp rise in copious external photoemission may itself actually reflect the valence to conduction band transition. It has been surmised[2] that the conduction band lies within a few tenths of an electron volt of the vacuum level, so this picture would be consistent with that. Measurements are currently under way to test some of these possibilities. One must recall here, of course, that metals show a similar sharp rise in quantum field at high photon energies.

The measurements reported here are at variance with those reported from this laboratory before the war.[14] It has been shown pretty clearly during the course of the present investigation, that considerable error was introduced in this earlier work in an assumed flat response for the silver photocell used to monitor the incident light, and more serious, in the neglect of the effects of scattered light which certainly contaminated the radiation, assumed monochromatic. These effects combine with the variation in lamp intensity with wavelength to explain the puzzling spectral response obtained. That a positive result was obtained at all for the photoconductivity was probably caused by similarly appearing currents induced instead by the copious photoelectric emission from metallic electrodes illuminated by light reflected to them by the crystal. These effects have all been a source of difficulty in the present work and fit well with what can be learned of the earlier work to explain those results.

SPECTRAL DEPENDENCE OF THE PHOTOELECTRIC YIELD

The external photoelectric yields on large single crystals were made as follows in the basic apparatus already described. Optical-quality Harshaw single crystals, approximately 10×10 mm, were cleaved to a thickness of

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

about 1 mm under an infrared lamp. The crystals were attached to a quartz frame with Duco cement and had a 3-mil copper wire attached to the back-surface silver-painted electrode by means of a drop of silver paint. The front surface, on which the light beam would be incident, was the freshly cleaved surface. While still warm, the crystals were installed in the apparatus and the detector head was evacuated. For the photoemission spectral response curves, data were taken at each of many wavelengths, at each wavelength the external collector electrode being raised to a potential of +400 volts. The electrode on the back surface of the crystal was used as the sensitive lead to the electrometer and thus held essentially at ground potential. In order to make a measurement of the photoemission current, the light shutter was opened and left open until the galvanometer deflection had reached its maximum and paused momentarily before starting its decay as the crystal surface charged to the collector potential. Following this measurement, the electrometer grid lead was grounded and, by turning the crystal and its mounting frame out of the path of the beam, the light intensity was measured with the phosphor-coated photomultiplier. The external collector electrode was then grounded, the crystal was turned back into the beam and discharged photoelectrically by electrons emitted from the electrode. This was done by reflecting from the crystal surface the diverging beam from the central image of the entrance slit back onto the external electrode and thus collecting on the crystal electrons released by the metal. The exit slit was then closed and the whole set of measurements repeated at the same wavelength. Thus each datum point is the average of at least two consecutive readings. If two consecutive readings taken at the same wavelength differed by more than 20% from each other, more readings were taken until the estimated standard error of all readings taken at that point were 20% or less. The reasons for deviations of even this amount are not certain, since when the dependence of the readings was checked at several wavelengths as a function of the collector voltage, the magnitudes of the currents were found to saturate at about 50 volts. Larger voltage merely kept the readings at their values for longer times, the crystal taking longer to charge up to the potential of the collector. Consistent with this was the fact that the decay of the signal was slower when the weak lines of the spectrum were used. The greatest fluctuations were observed for very small readings, on the order of 10^{-14} amp, which represented the inherent noise level of the electrometer tube as used.

Data on any given sample were taken by starting at low photon energies and working toward higher photon energies to minimize any effect through possible production of F-centers; successive runs on the same crystal duplicated within the errors of measurement, so no permanent effect of irradiation with the high-energy photons was observed. Data were corrected for scattered light in the manner previously described. Some runs on KCl were taken with a CaF_2 filter in the beam, thus making the scattered light corrections less important in the region of low photon energies. Corrected data obtained with and without the filter agreed with each other within the errors of either method.

In order to check the relative behavior of single crystals and evaporated films, some sample-holders were made up in which the crystal was replaced by a piece of nickel. The nickel was cleaned electrolytically, rinsed in distilled water and alcohol, and placed in the evaporator where it was outgassed for 30 minutes at about 400°C by means of the nichrome heater placed directly behind it. After the nickel had cooled, approximately 10 000 A of alkali halide was evaporated onto the front surface from powder contained in a heated tantalum boat. The powder was obtained by pulverizing scraps of Harshaw optical-quality crystals. The thickness of the evaporated films was judged during evaporation by watching interference fringes as they appeared on a glass slide placed near the nickel substrate. Following evaporation, the sample was again heated to 400°C to stabilize the film. After cooling, it was removed and transferred to the detector head.

Continuous photoemission currents could be drawn from the evaporated films, since they were thin enough to have a reasonably high dark conductivity. It was found that with these films even the largest currents saturated with 10 volts on the external collector electrode, but data were taken with $22\frac{1}{2}$ volts on the collector, to insure that all currents measured were saturated.

Data were taken on three KCl crystals, one NaCl single crystal, one CsI single crystal, two evaporated

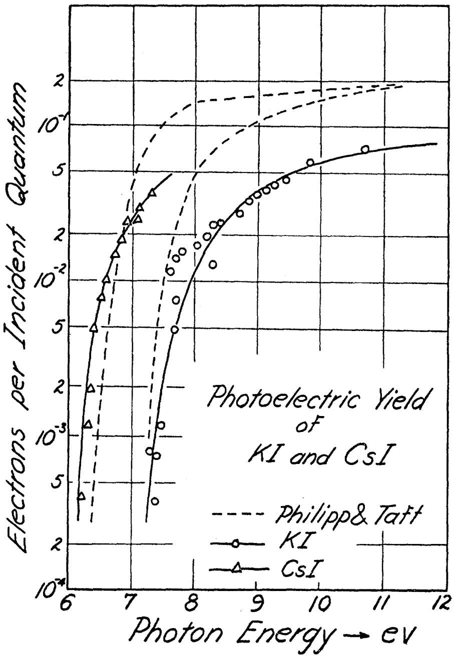

FIG. 4. External photoelectron yield curves for KI and CsI with comparison of curves obtained by Phillip and Taft.

films of NaCl, two of KCl, one of KI and three of LiF. Some data were also taken on a single crystal of LiF in a manner slightly different from the above. This crystal was fastened with Duco cement directly over the exit slot of the cylindrical electrode held at negative potential and all openings around it sealed to prevent the escape of any electrons out into the detector head region from the surface on which the beam was incident. Photoelectrons leaving the surface from which the light beam emerged were collected by a nickel plate immediately adjacent to this surface and grounded through the electrometer. These latter data were normalized to unit transmitted beam intensity. The measurements in this case were ballistic since steady-state currents were not obtained from the crystal. Thus the surface of the crystal had to be made negative following each measurement.

The results on KI and CsI are not new, but it was thought worthwhile as a check on the work to make the measurements to compare with the results of Phillip and Taft.[15] The agreement as indicated in Fig. 4, is seen to be reasonable.

In spite of the questionable procedure of removing the thin films, after evaporation, from the vacuum to install in the detector head, the agreement between the results obtained from single crystals and evaporated films of NaCl and KCl is seen from Figs. 5 and 6 to be quite good, except for one evaporated film of NaCl which does not reach the usual high yield. However, this film had a more cloudy appearance than the others, which may have been a factor.

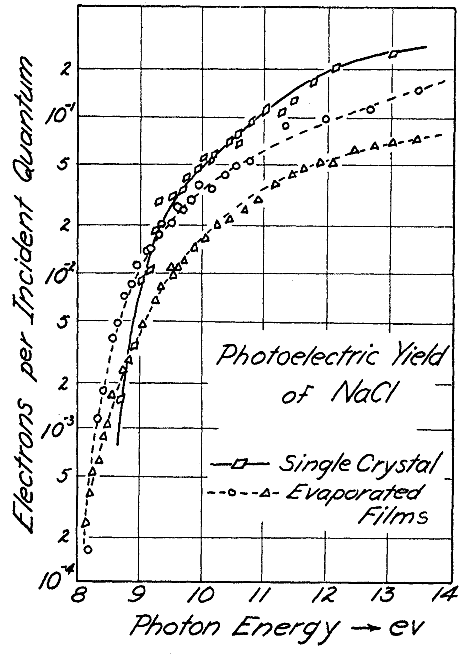

FIG. 5. External photoelectron yield curves for NaCl.

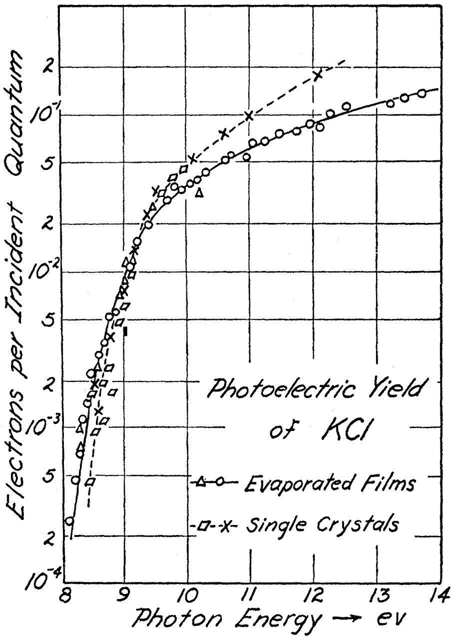

FIG. 6. External photoelectron yield curves for KCl.

The ordinates of all these curves are actually adjusted by assuming that the photoelectric yield of gold reaches 2×10^{-1} electron per incident quantum at 12 ev and by using this point to calibrate the photomultiplier and phosphor. Such an assumption was possible using known data on nickel[16] and making comparison measurements between nickel and gold. It leads to yields for CsI and KI which agree within a factor of two with the results of Taft and Phillip.

The yield obtained from LiF is indicated in Fig. 7. Measurements for this were made on two films evaporated from tantalum boats, one onto a nickel base and the other onto gold. A third film was evaporated from a platinum boat onto a gold base because it was feared that the tantalum might be combining chemically with the LiF and affecting the results. (After evaporation from the tantalum boat, the latter was quite discolored.) Since LiF is transparent for photon energies less than 12.5 ev, and since nickel is an efficient photoemitter in this region, there could be some concern that the apparent yield in this region was because of the substrate. However, the films all behave similarly and one of them was 100 000 A thick, so it seems difficult to believe that the relatively high yield obtained in this region could possibly arise from the substrate. This would imply that the yield per absorbed quantum is 10^{-1} or greater in this region of the spectrum, since the absorption coefficient of LiF at 1215 A is only about 1 cm^{-1}. The datum points at quantum energies greater than 14 ev were obtained with the helium discharge and are less precise for reasons explained earlier.

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[15] H. R. Phillip and E. A. Taft, J. Phys. Chem. Solids **1**, 159 (1956).

[16] K. Watanabe and H. E. Hinterreger, J. Opt. Soc. Am. **43**, 604 (1953).

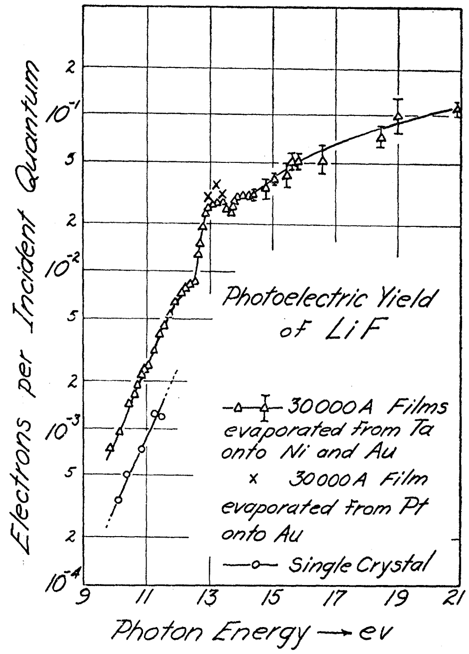

FIG. 7. External photoelectron yield curves for LiF.

It was not considered necessary to correct the photoelectric yields of NaCl and KCl for the high reflectivity these substances show in the region of their absorptions. Although the reflectivities are quite high (as indicated in Fig. 12), they do not vary enough as a function of photon energy at room temperature to do more than move the photoelectric yield data up and down by quantities which are about of the order of the uncertainties in these points. Inspection of an unpublished reflectivity curve taken for LiF by J. R. Nelson leads to the same conclusion as regards the data for this material. If the photoelectric yield of LiF in the region of photon energies between 12 and 14 ev were corrected for reflectivity, the structure in the yield curve would be but slightly enhanced.

Some of the threshold energies for photoemission are given in Table I. The 8.3-ev threshold for NaCl and KCl will be seen to occur at a position in the reflectivity spectrum at 1490 A, or at the position of the slight knee on the high-energy side of the lowest energy peak in Fig. 12. Any real correspondence between the two might be better shown by taking photoemission data at liquid nitrogen temperature. This has not yet been done.

TABLE I. Threshold energies for photoemission.

Salt	Observer	Threshold, ev
Film KI	Phillip and Taft	6.4
Film KI	Present work	6.2
Film CsI	Phillip and Taft	7.3
Crystal CsI	Present work	7.2
Crystal NaCl	Present work	8.5
Film NaCl	Present work	8.1
Crystal KCl	Present work	8.4
Film KCl	Present work	8.1
Film LiF	Present work	12.0?

ENERGY DISTRIBUTION OF THE PHOTOELECTRONS

The spherical collector and associated apparatus, which have been described earlier, were used to make retarding potential measurements on evaporated films of NaCl and KCl. Two samples of each substance were investigated, and all samples were similarly prepared.

The nickel substrate was cleaned electrolytically, washed in alcohol, and outgassed for half an hour at 450°C in the evaporator at a residual pressure of about 10^{-5} mm Hg. This was allowed to cool to room temperature and the alkali halides, again obtained by powdering Harshaw single crystals, were evaporated from a tantalum boat, which had previously been outgassed and cleaned. The samples were then transferred to the monochromator, and, without admitting residual hydrogen gas from the lamp to the system, they were first annealed and stabilized by heating to 450°C for half an hour and allowed to cool to room temperature. Film thicknesses were between 10 000 and 20 000 A, estimated from the interference fringes formed on a glass slide coated at the same time as the nickel substrate.

Retarding potential measurements were made as follows: The appropriate line of the hydrogen spectrum was made incident on the film, and the current reaching the spherical collector electrode was measured with the vibrating reed electrometer as a function of the potential of the nickel, which was varied in steps of 0.05 volt. It was found that the currents reached a maximum and became constant for accelerating potentials greater than 0.4 volt, except when the light intensity was too great. For example, when the 1215 A line was used at greatest intensity, it was found that the currents never saturated at voltages as great as $22\frac{1}{2}$ volts. The light intensity was therefore kept sufficiently low (by use of the weak dc "keep alive" lamp only) in all measurements so that this effect did not occur. It was concluded that the saturation was caused by the fact that the conductivity of the films was of the order of 10^{-11} ohm^{-1}, so that currents of the order of 10^{-11} amp and larger could cause appreciable potential drop through the films. Accordingly, the intensity of the light was adjusted so that the maximum currents taken from the films was of the order of 10^{-13} amp or less. This confirms the experience at the General Electric Research Laboratory on similar films.[17] This restriction is not inconvenient, since the electrometer would detect 10^{-15} amp accurately, reproducibly and reasonably quickly.

During the course of the measurements it was necessary to replace the nickel substrate, and although the second substrate was treated in the same way as the first, it was found that all subsequent retarding potential

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[17] Private communication from L. Apker and members of his group.

curves were shifted so that the saturation voltage was now 1.1 volt instead of 0.4 volt. The retarding potentials at which the currents approached zero shifted by the same amount in the same direction. It was concluded that the effective work function of the nickel had in some manner been changed.

In each series of measurements, the ratios I/I_0 of all currents, I, to the maximum current I_0, were plotted as a function of the retarding collector potential relative to the emitter. The curves which showed the displaced saturation value were moved on the voltage axis to coincide with the first set of measurements. In Figs. 8 and 9, the solid triangles are data from the first sample studied, and the open circles are from the second sample studied.

Because the data are fairly scattered, and because both samples were thought to be equally representative of the salt in question, a graphical average of the data from the two different samples was taken for each photon energy and the resulting curve was differentiated.

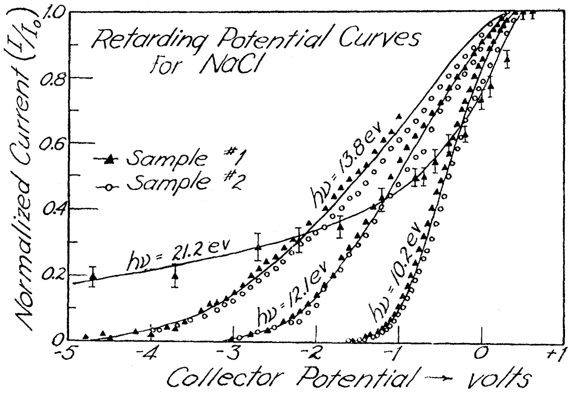

FIG. 8. Retarding potential curves for NaCl at four energies of irradiating photons. Currents I are normalized to the maximum current I_0 obtained at the corresponding photon energy. The bars through the helium line (21.2 ev) points reflect the uncertainty brought about by the lamp fluctuations occurring with the helium use.

The differentiated curves were integrated by Simpson's rule and the results were found to agree with the the initial curves within 2%. Because of this method of treatment of the data, no attempt was made to assign uncertainties to the points on the differentiated curves. The uncertainties in the points on the original curves are of the order of 2%, but in making the smooth graphical average curve, minor undulations in the differentiated curves were certainly introduced. Such variations do not, however, influence the main features of the electron energy distribution curves, since we are primarily interested in the maximum energy of electrons emitted when the sample is irradiated with photons of a particular energy, and the energy with which the majority of the photoelectrons emerge.

Figures 10 and 11 show the number of electrons per incident light quantum per electron volt of kinetic energy plotted against the energy of the electrons from NaCl and KCl at four different photon energies. The "zero" of the high-energy tail of each of these curves actually corresponds more nearly to the maximum energy for about 99% of the electrons. For NaCl and KCl one finds the results summarized in Table II.

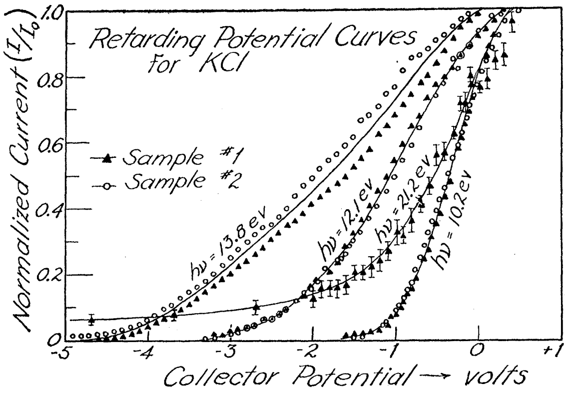

FIG. 9. Retarding potential curves for KCl at four energies of irradiating photons. Currents I are normalized to the maximum current I_0 obtained at the corresponding photon energy. The bars through the helium line (21.2 ev) points reflect the uncertainty brought about by the lamp fluctuations occuring with the helium use.

The results indicate that in both salts, most of the photoelectrons originate in a band of energy levels lying 8.3±0.1 ev below the vacuum level. This conclusion is consistent with the spectral dependence of the photoelectric yield for these salts, if one assumes that the electrons are coming from the valence bands. This latter conclusion is necessary because it seems that only the valence band could be sufficiently densely populated to produce the high yields which are observed.

It is to be noted that in the case of electrons ejected by the use of 21-ev photons, the majority of the electrons emerge with a very low energy. This behavior is

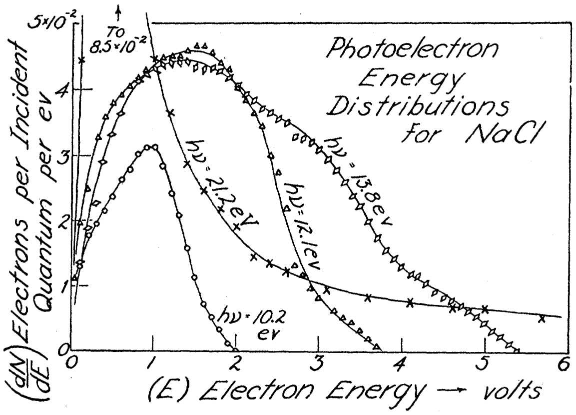

FIG. 10. Energy distributions of external electrons emitted from NaCl for four photon energies. The curves are obtained by differentiation of curves in Fig. 8.

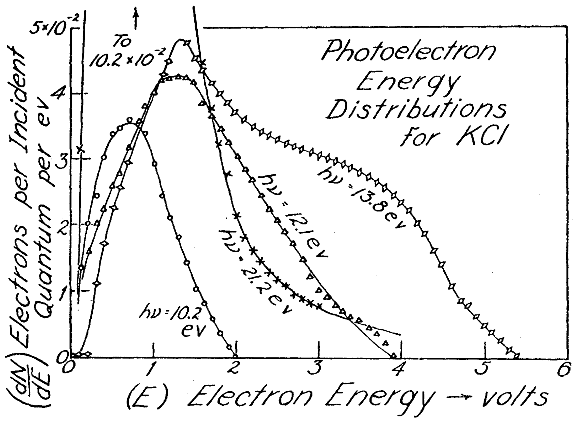

FIG. 11. Energy distributions of external electrons emitted from KCl for four photon energies. The curves are obtained by differentiation of curves in Fig. 9.

similar to that in Cs_3Sb.[18] One imagines that the electrons lose energy inelastically in emerging from the surface. For photon energies greater than twice the band gap, the concentration of electrons in the low-energy region will increase markedly at the expense of the concentration in the high-energy region.

DISCUSSION

The data on the external photoemission yields and on the energy distributions of emitted electrons presented in the preceding are consistent with a valence band position about 8.3 electron volts below the vacuum level in both NaCl and KCl. While this figure is at some variance with computed values of about 10.5 ev for the energy difference between the top of the Cl^- $3p$ band in these salts and the vacuum,[19,20] it is of interest to attempt interpretation of the known reflectivity and absorption curves for these salts previously referred to.[4] The room temperature reflectivities for both salts are replotted together as a function of photon energy in Fig. 12.

Consider first KCl. One is inclined to call the dip in reflectivity following the low-energy peak, presumed to be due to exciton formation, as caused by just the variation in the real part of the refractive index. If the effect of this is subtracted from the low-energy side of the second peak at 9.5 ev, the latter would have its rise moved to about 8.5 ev, roughly that where electron emission starts. The peak then occurs for that energy for which the product of the densities of states and their corresponding transition probabilities has its maximum. The energy at which the peak occurs is not to be taken as the gap width, now assumed to be 8.3 ev between valence band and the vacuum. The 1.5-ev difference between the high-energy foot of the peak and the onset of emission might then be interpreted as a possible width of the valence band. The third maximum in KCl at 12.7 ev would go unidentified at the present time.

TABLE II. Photoemission results.

Photon energy	Maximum electron kinetic energy (ev)		Difference (ev)	
	NaCl	KCl	NaCl	KCl
10.2	2.0	2.0	8.2	8.2
12.1	3.8	3.9	8.3	8.2
13.8	5.7	5.7	8.4	8.4

Against this sort of interpretation, however, is the fact that the photoelectric emission curves show no structure after the onset of emission to correlate with any of these optical variations. Furthermore, in this view NaCl presents additional difficulty in that its reflectivity shows no large sharp maximum within an electron volt or so of the exciton peak as does KCl. One might argue that this shows the valence band to be so wide as to smear it out. But this does not seem consistent with the observed equal depths below the vacuum for the valence bands in each. In this connection it is of interest and perhaps not unrelated that some recent unpublished measurements made here of the absolute absorption constants of NaCl and KCl indicate that NaCl has four or five times the absorption of KCl.

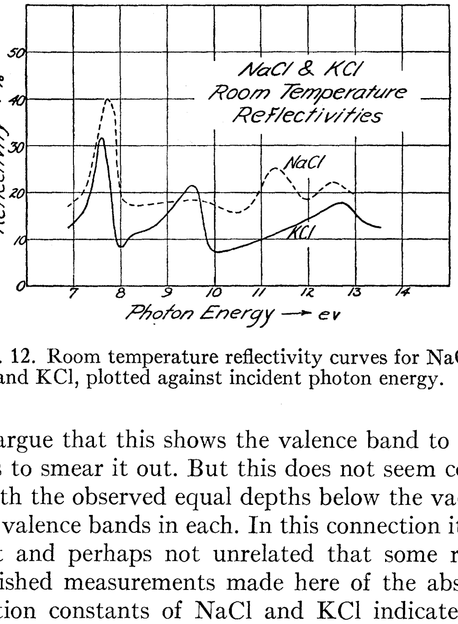

FIG. 12. Room temperature reflectivity curves for NaCl and KCl, plotted against incident photon energy.

The fact that photoconductivity is not observed anywhere over the spectral region investigated, one believes, is not because such transitions are not allowed, but rather that some particular phenomena associated with the very high absorption constants of the salts and hence excitation of free electrons very close to the surface, and perhaps an exceedingly short lifetime for the free carrier, is responsible for the conductivity not being found.

In summary, probably the best that can be said at the present time, is that there is little correlation between the observed optical and electrical properties of NaCl and KCl and that clarification between them still awaits

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some rather more subtle or refined and complicated techniques than have thus far been employed.

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"Thin-Film" Experiment with Bulk Superconductors*†

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Hollow cylindrical samples of indium have been prepared by an extrusion process and equipped with both a center wire and a concentric tube. The critical current has been determined for the case in which the current passes through the sample and returns through the concentric tube. It has been found that this critical current is identical with that of solid samples. The same determination has been made for the case in which the current returns through the center wire. In this case the critical current is about 80 to 90% of that for solid samples. A field was produced by the center wire, the respective current returning through the concentric tube. The resistance of the sample was measured with a small measuring current, also returned through the concentric tube, as a function of the field produced by the center wire. The critical field thus determined depends on the value of the measuring current. These findings can be interpreted in the following way: If the magnetic field of the current through the center wire is dominating, the current in the sample will flow in a very thin layer at the outer surface of the sample. This constitutes a "thin film experiment" which does not require a thin metal film. The resistance measurements have been supplemented by measurements of the circular flux on a sample of larger size.

I. INTRODUCTION

In the course of the investigation of the paramagnetic effect in superconductors,[1–7] it became apparent (see reference 7) that a number of differences between the present theory (see references 1 and 2) and the experimental results could be resolved if the mean value of the magnetic field between the superconducting domains would be different from the bulk critical field. A calculation of this field in the light of any of the existing theories of superconductivity[8–12] requires a knowledge of the size of the superconducting domains. The principles governing the size of the domains are unfortunately not yet known. Good fortune[13] brought to the attention of the authors an arrangement which seems to be of interest in this connection. The arrangement consists of a sample in the shape of a hollow cylinder, provided with a wire through the center and a concentric tube (see Fig. 1). The current can be passed through the sample and returned either through the center wire (this connection is denoted as "wire") or

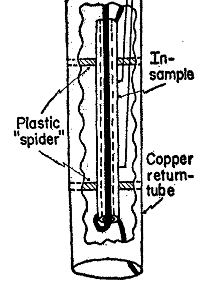

FIG. 1. Hollow cylindrical sample for resistance measurements.

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† A preliminary account was given in the *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), Paper 9-5.

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