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Primary Photocurrent in Cadmium Sulfide

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Experiments were performed on the photocurrent caused by short flashes of light and by individual α particles in high-resistivity cadmium sulfide crystals. It was shown that the photocurrent pulses could be described by the mechanism of the so-called primary photocurrent of both electrons and "holes." The energy lost by an α particle per electron-hole pair created was found to be 7.2 ev, which seems somewhat high. Efforts to correlate the primary photocurrent with the so-called edge luminescence were not successful.

1. INTRODUCTION

When an electric field is applied to a photoconductor and it is irradiated by light of the proper wavelength, a number of electrons and holes will be formed which will drift in the electric field until they become trapped or reach the electrodes. This is the primary photocurrent which was defined by Pohl and observed by him and his school in the classical work on diamond and zincblende,[1] the alkali halides,[2] and the silver and thallium halides.[3] At least in one substance, zincblende, the motion of the positive charge, or what we now call holes, was also observed.

When the substances are irradiated with corpuscular radiation or x-rays, again electrons and holes will be formed in it, leading to a current completely analogous to the primary photocurrent, and in this article for brevity's sake it will be called by that same name. Accordingly, in the forties, all these substances known to show primary photocurrent were also demonstrated to show primary photocurrent pulses for individual α, β, or γ rays.[4] In this way McKay[5] found a primary hole current to be present in diamond in addition to the primary electron current. On the other hand, Brown[6] found no evidence of a hole current in silver chloride.

Relatively pure cadmium sulfide is a good insulator and therefore may be expected to show a primary photocurrent in a pure form. Indeed Frericks and Warminsky[7] demonstrated the presence of current pulses due to corpuscular radiation, but here the confusion arises that some CdS samples give current pulses much too large to present a primary current pulse only. This was realized by Kallmann and Warminsky,[8] who pointed out that the larger pulses, which must be caused by secondary effects, occur in crystals which have a large impurity content. They demonstrated what looks very much like a primary current, however, in pure cadmium sulfide. The current pulses due to α particles were very fast, uniform, proportional to the energy, and of the right order of magnitude. However, since the phenomena in CdS are obviously complex, one has to be careful and would like to make sure that it is really a primary photocurrent. Now a property of the primary current is that it is linear with voltage on the sample for low voltages and saturates for higher voltages ("Hecht curve"[3]). This is a piece of information missing in reference 8. A second point is that the energy spent by corpuscular radiation per electron-hole pair generated is a material constant independent of the kind or energy of the radiation. McKay[9] tentatively gives a universal empirical formula for this amount ϵ given by $\epsilon \cong (E_g + 2.5)$ ev, where E_g is the distance between valence band and conduction band. This is another thing one would like to know and which is missing in the Kallmann and Warminsky article since they did not calibrate the amplifier in units of charge.[9] However, if one estimates the input capacity of their amplifier to 30 $\mu\mu f$ one calculates for ϵ in CdS the value 6 ev, while McKay's formula gives 5 ev, and this therefore gives reasonable agreement.

Kolb[10] has performed interesting experiments on current pulses by α particles in very thin CdS crystals. He finds that the size of the current pulses depends on the side from which he bombards the crystal, the positive or the negative electrode. For large voltages, however, the asymmetry disappears. He explains this with the hypothesis of a nonuniform electric field in the crystal, but it seems much more simple and straightforward to explain this by the occurrence of both a primary electron and a primary hole current: if the drift range in unit field S_0 is smaller for holes than for electrons, then smaller pulses will be observed when we bombard from the negative electrode, as long as the penetration of the α particles is less than the crystal thickness. For higher voltages, however, the primary hole current also saturates and the asymmetry disappears. When one accepts this explanation for Kolb's observations, one can estimate that in his crystals S_0 for holes is between 10^{-7} and 10^{-8} cm^2/volt.

In view of the above it seemed worth while to supplement the observations of these authors and clear up

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[1] B. Gudden and R. W. Pohl, Z. Physik **16**, 170 (1923); **30**, 14, (1924).

[2] R. W. Pohl, Physik. Z. **39**, 36 (1938).

[3] K. Hecht, Z. Physik **77**, 235 (1932); W. Lehfeldt, Nachr. Ges. Wiss. Gottingen **171** (1935).

[4] R. Hofstadter, Nucleonics **4**, No. 4, 2–27 (1949); 4, No. 5, 29–43 (1949).

[5] K. G. McKay, Phys. Rev. **74**, 1606 (1948); **77**, 816 (1950).

[6] F. C. Brown, Phys. Rev. **97**, 355 (1955).

[7] R. Frericks and R. Warminsky, Naturwiss. **33**, 251 (1946); 33, 281 (1946).

[8] H. Kallmann and R. Warminsky, Research **2**, 389 (1949).

[9] K. G. McKay, Phys. Rev. **84**, 829 (1951).

[10] W. Kolb, Ann. Physik **14**, 398 (1954).

these questions left by them. Accordingly, CdS crystals of high resistance were irradiated in our experiments through either one of the thin electrodes with light or α particles. When the thickness of the crystal is large with respect to the depth of penetration of the radiation, one expects to observe essentially a pure primary electron current when this electrode is the cathode, and a primary hole current when it is the anode.

2. EXPERIMENTS

The CdS crystals were obtained from different sources, but all were platelets from 20–200 microns in thickness and a few mm^2 in area. The resistivity of all was higher than 10^{12} ohm cm. Gold electrodes, about 0.1 micron thick and 0.8 mm in diameter, were evaporated on opposite sides. Figure 1 gives the experimental setup. A General Electric mercury flash lamp "photolight" was used as a light source; it gives light flashes a few microseconds long. The light was filtered by an interference filter combined with Corning filter 4303 to select the 4580 A mercury line, which is absorbed in a layer of 1000 A. From data on other materials[11] the α particles were estimated to have a penetration of 20 microns with the average charge carrier generated at a depth of 12 microns. The current pulses were amplified by a simple Elmore model 50 preamplifier[12] and fed into a Tektronix 535 oscilloscope with 53B preamplifier. Charge calibration pulses were obtained from a Tektronix 104A square-wave generator (rise time 0.02 μsec) on a 0.6-$\mu\mu f$ consenser connected to the input of the preamplifier. The rise time of the calibrating pulse on the scope was 0.06 μsec.

With this arrangement, the current pulses caused by flashes of light and individual α particles were observed. The pulses from α particles in many samples were not as uniform as one would expect from perfect crystals. The homogeneity in the best samples was 20–30% of the total height. The pulses due to hole current, with the irradiation at the side of the crystal of negative bias, were always less homogeneous than the electron current pulses. In this article, pulse height for α particles therefore will always mean maximum peak height. The current pulses due to light were always much more uniform and variations in it were due only to variations in the light sources. Furthermore, the pulse height varied from sample to sample. In some crystals, for instance, no hole current at all was observed, indicating an extremely short lifetime for holes. With these facts in mind, a few curves are given in Fig. 2 for the pulse height *versus* bias voltage both for light flashes and α particles in the same crystal for some of the best crystals. No effort was made to bring a theoretical "Hecht curve" through the experimental points, but they demonstate in a qualitative way the two main points of the investigation, which are (1) that the electron current is linear with bias voltage for low voltages and becomes saturated for higher voltages, and (2) that there is a hole current which is linear with voltage and which has not reached its saturation value.

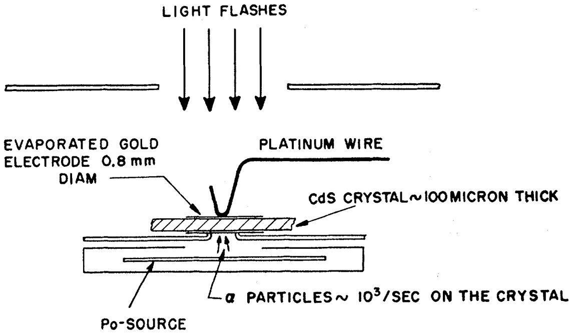

FIG. 1. Holder for CdS crystals.

The penetration of the light in the crystal is negligible with respect to the thickness of a crystal, and therefore one should observe a pure electron or pure hole current for negative or positive bias on the irradiated side. For α particles there is a "mixing" of about 15%, since the average depth of formation of an electron hole pair is about that percentage of the total thickness. The hole current observed, however, is definitely too large to be explained by this effect.

From the slope of the bias curve at small bias one can derive the quantity S_0, the "schubweg" in unit field. In the samples of Fig. 2 this varies between 2×10^{-7} to 8×10^{-7} cm^2/volt for electrons, while for holes this value is 10^{-8} to 10^{-7} cm^2/volt, a factor of 10 lower. This is the same value as one can derive from Kolb's experiments if one accepts the explanation discussed before.

S_0 can be expressed[5] in the mobility μ and the lifetime for trapping τ: $S_0=\mu\tau$. Therefore, if the lifetime were known, we could derive the mobility from these measurements. Now the lifetime can in principle be derived from the rise time of the pulse,[6] since the pulse shape represents the integrated current, the charge collected on the plate, as a function of time. This is so provided the electron hole pairs are all formed in a very short time, which is true for α particles. In most samples investigated, however, there was no observable difference in rise time between the α-particle pulses and the calibration pulses. With the attainable accuracy this means that the lifetime of the electrons and holes is smaller than 0.04 μsec. This therefore leads to a lower limit for the mobility: for electrons $\mu_e > 5$–20 cm^2/volt sec, and for holes μ_h is about ten times smaller. It is probable, however, that it is not so much the mobility as the lifetime which differs for electrons and holes. If we assume the value $\mu_e=210$ cm^2/volt-sec, recently determined from the Hall effect,[13] one can calculate the lifetime of the electrons in our samples to be 0.004–0.001 μsec.

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[11] G. W. Gobeli, Phys. Rev. **103**, 275 (1956).

[12] W. C. Elmore and M. Sands, *Electronics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 161.

[13] Kröger, Vink, and Volger, Physica **20**, 1095 (1954).

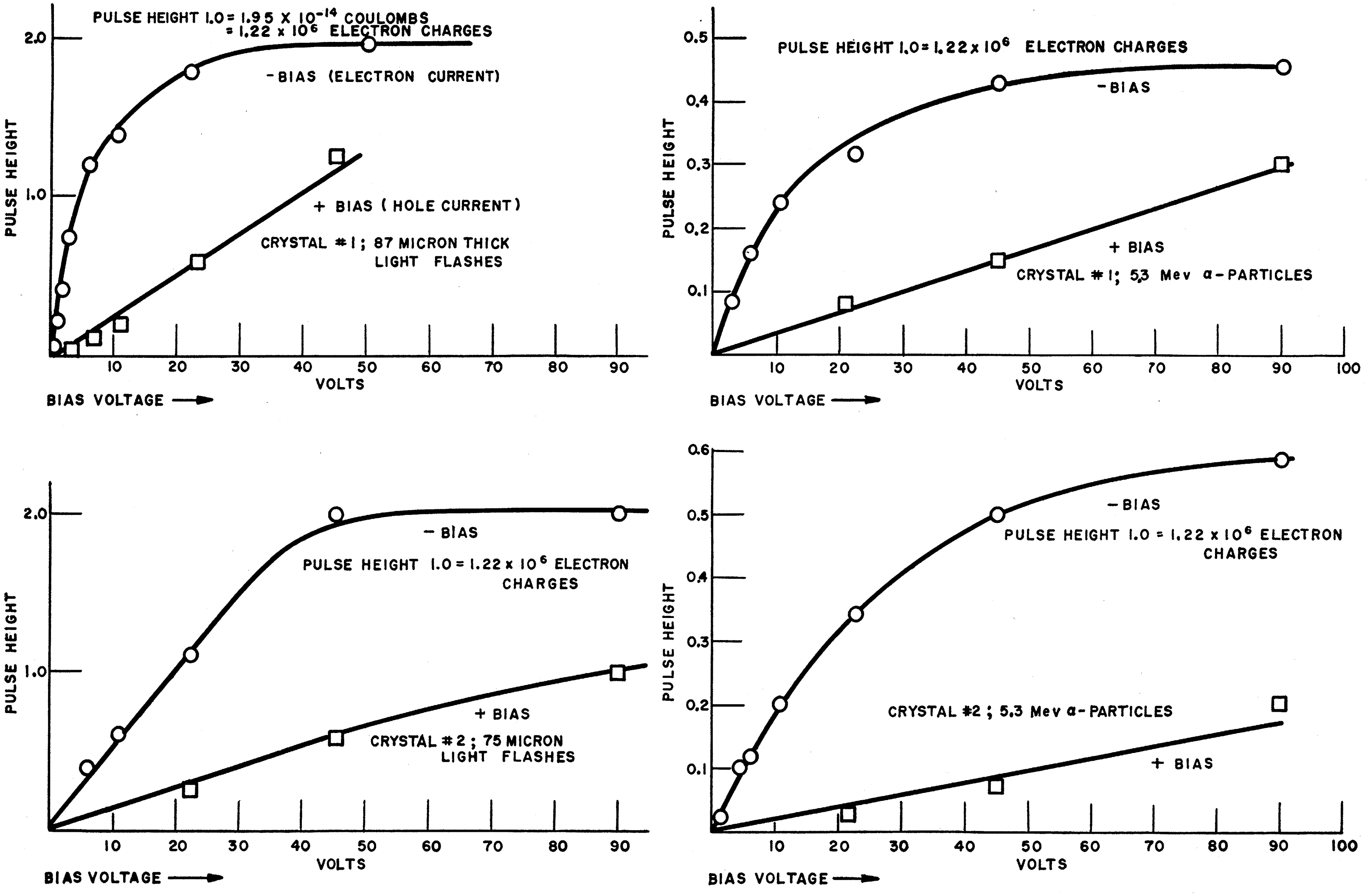

FIG. 2. Primary current in CdS from light flashes and α particles.

From the saturation value of the primary electron current for α particles one can derive the value of the amount of energy ϵ required to generate an electron hole pair, which was discussed before. From the curve for crystal No. 2 one arrives at the figure $\xi = 7.3$ ev, which is somewhat higher than the value of 5 ev one would expect from McKay's empirical formula.

Since the lifetime of the electrons is probably so much longer than that of the holes, one would still expect a response to a light flash for zero bias, a *photovoltaic effect*. The electrons generated by the light flash will diffuse both ways, but since they are generated within 1000 A from the electrode, the ones moving in that direction will disappear into the electrode and cause no movement of charge, while the ones diffusing into the crystal will show a net effect. A calculation shows that the ratio of the photovoltaic pulse to the pulse at saturation bias is given by

$$(S_0kT/e)^{\frac{1}{2}}/d,$$

where d is the thickness of the crystal. Substituting, for instance, $S_0 = 8\times 10^{-7}, kT/e = 2.5\times 10^{-2}; d = 87\times 10^{-4}$ cm, one finds this ratio to be about 0.02, i.e., the photovoltaic pulse should be 1/50 of the saturation pulse. This would be just at the threshold of observation. A few times such an effect (always of the right sign) was observed, but it was not very reproducible and therefore cannot be claimed with certainty.

There is one difficulty in the understanding of α-particle pulses which is far from explained. The electron hole pairs, about 10^6 in number, are generated in a very small volume around the track of the α particle. When these charges begin to separate under the action of the bias field, an electrostatic interaction will be set up between the cloud of holes and the cloud of electrons which seems higher than the bias field itself. Consider, for instance, the 5×10^5 holes over a part of the track of 10 microns. At a distance of 10 microns this will exert a field E approximately given by $E = ne/kr^2 = 5\times 10^5 e/[k(10^{-3})^2] = 25$ esu $= 7500$ volts/cm, where k, the dielectric constant, is estimated to be 10. Now the saturation voltage of about 50 volts exerts a bias field E_b, where $E_b = 50/(85\times 10^{-4}) \cong 6000$ volts/cm. So how can these electrons escape at all the attraction of the holes under the influence of such a relatively weak bias field? The fact is, however, that the same objection holds against all experiments with α particles done up till now, and for instance certainly for the experiments done by McKay in germanium.[9] In practice, therefore, the electrons seem to escape more easily than one would expect from these estimates, although it is possible that the value for the energy required per electron hole pair of 7.2 ev which was found in our experiments is higher than the actual value because of this effect.

A possible explanation of this paradox has been offered by Redington[14]: Since at the moment of its formation the electron-hole cloud is neutral, electrons will be drawn away from it until the cloud becomes so positively charged that escape from it becomes difficult. But then this positive cloud as a whole will drift in the bias field towards the cathode, which is only 10 microns away. There the holes will be neutralized, so that now the electrons can escape unhindered. This explanation seems very reasonable in the light of the obvious discrepancy between experiment and theory which would otherwise exist.

3. CIRCUMSTANCES UNDER WHICH A PURE PRIMARY PHOTOCURRENT CAN BE OBSERVED*

In the experiments of Pohl and his school, photocurrents were observed which had a quantum efficiency much larger than unity and which had a time constant much longer than the expected transition time of a single electron through the sample.[3] Such currents were called secondary photocurrents by Pohl and the general idea of the explanation was the requirement of space charge neutrality: if, for instance, holes are trapped and electrons move out of the crystal, then the positive charge thus formed will attract other electrons and cause them to enter from the cathode and move through the crystal, and so the current will continue to flow until recombination takes place of electrons with the trapped holes. This idea has only recently received a firm quantitative experimental footing in the experiments of Tyler, Woodbury, and Newman on the photoconductivity in germanium[15] doped with the transition elements like Fe, Ni, Co, and Mn which act like hole traps of known depth and concentration. But especially the study of photoconductivity in low-resistivity semiconductors makes the old division between primary and secondary currents seem artificial and only of historical value. How is one ever going to tell experimentally when the primary photocurrent stops flowing and when the secondary current begins? For that reason it is useful to consider what conditions have to be satisfied so that one can expect to observe the primary current separately.

Consider (Fig. 3) a flat crystal with a voltage V_0 on the parallel electrodes and assume that the dark current in the crystal is purely ohmic, which means that the Fermi level of the electrode metal is exactly lined up with the Fermi level in the crystal; in this way no space charge regions or barrier layers occur. (In practice, an ohmic contact with n-type material is established with an electrode in which the Fermi level is higher than in the material. This is quite correct as long as the current resulting from the space charge, which is not ohmic, is negligibly small with respect to the ohmic current.)

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[14] R. W. Redington (private communication).

* *Note added in proof.*—During the proofreading it came to my attention that the considerations in this paragraph are practically identical with those of S. M. Ryvkin, Doklady Akad. Nauk S.S.S.R. **106**, No. 2, 250–253 (1956).

[15] Tyler, Newman, and Woodbury, Phys. Rev. **102**, 647 (1956); W. W. Tyler, General Electric Research Laboratory Report 55-RL-1334 (unpublished), and references.

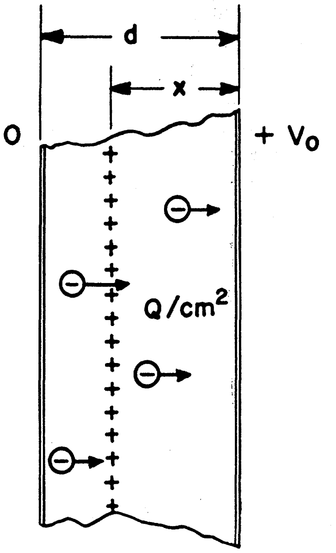

FIG. 3. The condition for primary photocurrent: $4\pi d/(\rho k\mu E)\ll 1$.

Moreover it will be assumed for simplicity that the current is only an electron current. The current per cm², j_0, is given by $j_0=V_0/d\rho=E_0/\rho$ and $1/\rho=n_0e\mu$, where, as usual, n_0 is the number of electrons per cm³ and μ is the mobility.

Now assume that at a distance x from the anode in a thin layer parallel to the electrodes and in a very short time, a number of electrons and holes are generated. The electrons will start moving to the anode while the holes are immediately trapped to form a space charge $+Q$ per cm². This space charge will induce an extra field at the cathode, causing more electrons to enter. We shall now calculate the extra current per cm², Δj, caused by this effect after it has obtained a stationary value which it will reach approximately in the time it takes the electrons to traverse the crystal.

Let the excess electrons present in the crystal in that case form a charge $-\alpha Q$. They will be distributed homogeneously over the crystal if we assume that the extra field caused by the charge Q is small with respect to E_0. Now the field E_0, originally acting at the cathode, is increased to a field

$$E=E_0+\left(\frac{x}{d}\right)\left(\frac{4\pi}{k}\right)Q(1-\alpha)$$

(in esu), where k is the dielectric constant of the crystal. The number of electrons N entering at the cathode per second and per cm² is given by $N=E\mu n$, and therefore the increase in electrons ΔN entering due to the space charge is given by

$$\Delta N=\mu n\left(\frac{x}{d}\right)\left(\frac{4\pi}{k}\right)Q(1-\alpha).$$

This leads to a current increase

$$\Delta j=\mu ne\left(\frac{x}{d}\right)\left(\frac{4\pi}{k}\right)Q(1-\alpha).$$

On the other hand, this extra current can also be given by considering the number of excess electrons flowing through an arbitrary plane parallel to the cathode, since the current is stationary. Therefore

$$\Delta j=(\alpha Q/d)\mu E_0.$$

From these two expressions for Δj one can calculate α, and it is found that

$$\alpha=\beta/(1+\beta),$$

where

$$\beta=4\pi xen\mu/(kE_0\mu)=4\pi x/(\rho kE_0\mu).$$

The primary photocurrent j_p, flowing during the short time it takes the primary electrons to reach the anode, is given by $j_p=E_0\mu Q/d$. Calculating now $\Delta j/j_p$, one finds that

$$\Delta j/j_p=\beta/(1+\beta).$$

It is clear that essentially two situations can occur depending on whether $\beta\gg 1$ or $\beta\ll 1$. If $\beta\gg 1$, $\Delta j\cong j_p$ and the "secondary" current Δj is practically equal to the primary photocurrent j_p. On the other hand, if $\beta\ll 1$ the "secondary" current is very small with respect to the primary photocurrent. Now $(\rho k/4\pi)$ is the relaxation time of the material, and $d/E_0\mu$ is the transit time, the time it takes an electron to traverse the crystal. Therefore, *a pure primary photocurrent will be observed if the transit time is small with respect to the relaxation time.*

In the case of the CdS crystals as they were investigated, $\rho=10^{12}$ ohm cm, $\rho k/4\pi=1$ sec. Also $d=10^{-2}$ cm; assume further that $V_0=1$ volt or $E_0=100$ volt/cm and $\mu=10$ (a minimum value); then $\Delta j/j_p=10^{-5}$. It is clear that in this case the condition for observing the primary current is very well satisfied. On the other hand, when CdS is doped with an impurity which forms donor centers and thus reduces the resistivity, the condition $\Delta j/j_p\ll 1$ may no longer hold. In fact, in our experiments, occasionally larger, slower pulses were observed under α-particle bombardment which clearly were not primary current pulses. They may have been due to small regions of lower resistivity near the cathode.

The "secondary current" pulses from α particles observed by Frericks and Warminsky[7] were irregular in shape and not uniform in height and not proportional to the energy. The reason for this is probably that to observe regular pulses of uniform height and proportional to the primary effect, the material near the cathode should be very homogeneous and moreover a good ohmic contact is required. A good possibility for studying this transition from primary current pulses to secondary pulses seems to be in copper-doped germanium, recently studied by Tyler and Woodbury.[16] Here a thin "transparent" ohmic contact layer can be made by diffusion of arsenic into a thin surface layer. At liquid nitrogen temperature the resistance is very high and the pulses should be pure primary current. At higher temperatures the resistance is sufficiently reduced to show secondary phenomena.

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[16] H. H. Woodbury and W. W. Tyler, Phys. Rev. **105**, 84 (1957).

4. CORRELATION OF PHOTOCONDUCTIVITY WITH EDGE LUMINESCENCE

Some CdS crystals show the so-called edge luminescence[17] while others do not. This edge luminescence is a light green luminescence under ultraviolet irradiation which shows up only when the crystal is cooled to liquid nitrogen temperature. Since the primary process in both photoconductivity and luminescence is the generation of an electron hole pair, it was thought that there might be some correlation between these two phenomena. For that reason a few observations were made on this edge luminescence. First it was established that all crystals which showed edge luminescence under ultraviolet light also show this under x-ray irradiation, and vice versa. This means that the property of a crystal being luminescent or not is a volume effect, not a surface effect.

Next the edge luminescence scintillations caused by α particles in these crystals were observed with a photomultiplier tube. These scintillations have a rise time of about a microsecond, and therefore much longer than the primary photocurrent pulses. The maximum pulse was about 50 000 photons, corresponding to 1% efficiency. In the end, however, no correlation was found between the property of being luminescent and the photoconductive behavior of the crystals.

5. CONCLUSION

The observations on CdS by previous authors were supplemented to demonstrate that a primary photocurrent could be observed in insulating crystals. No correlation was found between this primary photocurrent and the presence of edge luminescence in these crystals.

ACKNOWLEDGMENTS

I want to thank J. M. Stanley of the Signal Corps Engineering Laboratories and W. W. Piper of this Laboratory for supplying me with samples of CdS crystals.

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[17] Lambe, Klick, and Dexter, Phys. Rev. **103**, 1705 (1956), and references.

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Temperature Dependence of Ion Mobilities in Helium, Neon, and Argon

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Measurements have been made of the temperature variation of the atomic and molecular ion mobilities in the parent gases, helium, neon, and argon over the range 77–300°K. The experimental values for the atomic ion mobilities are compared with calculations based on Holstein's theory. The results for neon and argon are in good agreement with the values calculated from the theory. This is in contrast to the case of helium where the experimental results lie consistently below the theoretical values. The molecular ion mobilities are compared with the temperature variation predicted by the Langevin and Hassé-Cook theories. The experimental results in neon and argon lie intermediate between the predictions of the two theories in agreement with expectations; however, the helium data cannot be reconciled with either of these theories.

RECENTLY many of the apparent discrepancies among the various ion mobility measurements have been removed as a result of more precise measuring techniques and proper identification of the ions under study.[1–4] By using a mobility tube in which measurements with small applied drift fields are possible we have been able to measure the mobilities of ions moving with near-thermal (300°K) energies.[3] The experimental values have been compared with the recently developed theory for atomic ions moving in their parent gases[5] and good agreement has been found at 300°K.

If one wishes to make a more detailed comparison with theory by studying the energy dependence of the ionic mobilities, it is preferable to vary the temperature of the gas in which the ions drift rather than to increase the drift field to change the ion energy. This situation results from the fact that ionic drift velocities, unlike those of electrons, are very difficult to calculate when the ions depart from thermal equilibrium with the gas under the action of an applied electric field.[6] Thus, to facilitate comparison with theory we have confined our measurements to drifts in small electric fields and have varied the ion's energy by varying the temperature of the gas in which they move.

I. METHOD OF MEASUREMENT

The mobility tube used in these studies has been described in detail previously.[3] The tube, which is shown schematically in Fig. 1, consists of a shielded

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[1] J. A. Hornbeck, Phys. Rev. **83**, 374 (1951).

[2] R. N. Varney, Phys. Rev. **88**, 362 (1952).

[3] M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954).

[4] A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, New York, 1938).

[5] T. D. Holstein, J. Chem. Phys. **56**, 832 (1952).

[6] See, for example, G. Wannier, Bell System Tech. J. **32**, 170 (1953), and Phys. Rev. **83**, 281 (1951).