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UNCOOLED IR DETECTOR
FOR THE TEN MICRON REGION

Chief, Bureau of Naval Weapons
UNCOOLED IR DETECTOR FOR THE TEN MICRON REGION

April 1, 1962, through December 31, 1962

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ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY
FOREWORD

This summary technical report under Contract NOw 62-0751-c describes the research performed from 1 April, 1962, to 31 December, 1962. The effort during this period was primarily directed toward the selection of CdS crystals which exhibit infrared quenching of exciton-induced photoconductivity, but during the latter months the emphasis shifted to more fundamental studies of exciton transport. Principal contributors to this report are W. D. Brennan, project leader, and J. Kroll. Data are recorded in logbooks 12415, 12567, 12569, 12632, 12804, 12805, 12808, 12824 and 12960.

Respectfully submitted,

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ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY
ABSTRACT

UNCOOLED IR DETECTOR FOR THE TEN MICRON REGION

This report summarizes the experimental effort carried out under Contract NOw 62-0751-c for the Bureau of Weapons during the period 1 April, 1962 to 31 December, 1962. The objective of this research program is to develop an uncooled infrared detector for the 8μ to 12μ atmospheric window. In contrast to all other quantum infrared detectors, the principle of operation of the proposed detector does not involve free carrier generation by the infrared radiation. Instead, the detector shall use the absorption of infrared energy by excitons to quench an exciton-induced photoconductivity.

In this report methods and techniques to observe exciton-induced photoconductivity and quenching by infrared radiation are discussed. During the course of the work some 90 crystals were examined, and while the quenching effect was never observed, 11 of these crystals appear to exhibit the required exciton processes.

The experimental procedures are being modified to emphasize the observation of exciton transport and to remove some interferences that might have inhibited or masked the quenching in previous experiments.
UNCOOLED IR DETECTOR FOR THE TEN MICRON REGION

I. INTRODUCTION

This summary report describes the results of research to explore the feasibility of using exciton absorption of infrared energy to develop a useful uncooled detector for the ten micron region. This work was done under Contract NOw 62-0751-c; this report covers the period April 1, 1962 to December 31, 1962 and represents the combined reports for that interval.

An exciton is an electron and a hole in a crystal bound together through their mutual electrostatic attraction and rotating about their common center of mass. The configuration of an exciton, then, is similar to that of a hydrogen atom, except that the electron and proton in a hydrogen atom exist in empty space where the dielectric constant is unity while the exciton moves in a material of high dielectric constant. It can be shown that the ionization energy of a hydrogen atom is inversely proportional to the square of the dielectric constant\(^1\), so one would expect that the ionization energy of an exciton (equivalent to the distance below the conduction band of the exciton ground state) in a typical semiconductor to be of the order of \(10^{-2}\) times the ionization energy of hydrogen. In cadmium sulfide early spectrographic measurements in which a regular absorption series (analogous to the fundamental series in hydrogen) was observed near the absorption edge suggested an exciton ionization energy of about 0.1 ev. Later measurements suggest a lower figure, about 0.03 ev\(^2\). Considering that the macroscopic dielectric constant of CdS is about 9.3\(^3\) and the ionization energy of hydrogen is 13.5 ev, the exciton ionization energy is in order-of-magnitude agreement with the hydrogenic approximation.

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It is apparent that an exciton is free to move through a crystal lattice and is unaffected by electric fields since its net charge is zero (except that a sufficiently high electric field can dissociate the exciton through a process similar to field emission). The exciton can be dissociated into a free hole and electron thermally or by absorbing a photon of energy greater than its ionization energy. For the two ionization energies mentioned above, 0.1 ev and 0.03 ev, the corresponding photon wavelength is 12.4 µ and 41 µ.

Although theoretically an exciton can move through a crystal and considerable experimental evidence has been amassed which supports the mobility of excitons, considerable controversy exists over whether excitons actually are as mobile as some of the experiments indicate. The papers by Diemer and his co-workers present strong evidence that photoconductivity observed between two contacts on crystalline CdS which are well removed from the illuminated region, can be partly due to the diffusion of exciton produced in the illuminated region. These excitons diffuse through the crystal to the region near the contacts where they are ionized thermally. In their papers the authors carefully consider the contribution which scattered light and fluorescence radiation can make to the photoconductivity; the only apparent conclusion is that excitons can be important in this long-range photoconductivity. Specifically, they conclude that the diffusion length of excitons can be several millimeters and their lifetime nearly 100 µ sec. Diemer's work has been vigorously, although unconvincingly, attacked. The opponents to the exciton transport theory have never explained all of Diemer's results with any non-exciton hypothesis.

Diemer noticed that this exciton-induced photoconductivity could be quenched by illuminating the crystal simultaneously with infrared light with any wavelength from 0.8 µ to 10 µ. Apparently the infrared energy ionized...
the excitons before they reached the contact region. Unless the free electron-hole pairs are formed near the contacts, they cannot contribute to the photoconductivity. This is due to the holes being trapped almost immediately, producing internal electric fields which prevent electrons from reaching the contacts. Only one of Diemer's twenty-five crystals exhibited this strong exciton diffusion and quenching phenomena. Subsequent work in these laboratories by R. J. Robinson confirmed the observation of infrared quenching of exciton-induced photoconductivity; Robinson observed the effect in one crystal out of seven selected for examination.

It is interesting to note that long-range photoconductivity similar to that described above has been observed in germanium\(^6\). During a discussion of this work (which was reported orally), it was suggested that the photoconductivity should be quenched by illuminating the crystal with infrared radiation\(^7\).

The experiments described above supplied the motivation for the present research. The objective of this effort under Bureau of Weapons sponsorship is to exploit this phenomena of infrared quenching to develop a useful uncooled detector for the 10\(\mu\) region. The entire effort during this report period was directed toward discovering crystals in which exciton-induced photoconductivity could be quenched by radiation in the 10\(\mu\) region. Despite the fact that approximately 90 crystals of CdS were examined during this period, many of them by several methods, the infrared quenching phenomena was never observed although in eleven of these crystals excitons are suspected of contributing to the photoconductivity. There is no reliable explanation for this adverse development; the optimistic view is that we are victims of statistics.

In the following sections the experimental effort conducted during this

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report period is described in detail.

II. EXPERIMENTAL WORK

A. Early Experimental Arrangements and Results

The initial experimental facility used a monochromater for spectral selection of light to generate excitons, while infrared radiation was obtained from a Nernst glower, filtered with a 0.005 inch InSb single crystal wafer. The InSb absorption edge is at approximately 6.5 μ, and its transmittance for wavelengths longer than 6.5 μ is approximately 30%. For some experiments a germanium wafer, 1 mm thick, was used as an IR filter. This crystal’s absorption edge is near 1.7 μ and its transmittance for longer wavelengths is 55%.

The use of a monochromater as a visible light source was dictated by the expectation that the efficiency of exciton production would be wavelength dependant. The data-taking procedure initially consisted of focussing the line of visible light at various distances up to several millimeters from the contacts and measuring the photoconductive response of the crystal while the wavelength of the incident light is varied from 400 to 700 μ. Then the infrared energy is allowed to fall on the crystal and the photoconductive response is remeasured. The photocurrents measured in this way are subtracted and plotted as a function of wavelength. Figure 1 shows the sample configuration during these measurements; for pictorial clarity the visible and infrared light is shown incident on the same crystal face, while in practice these two beams were incident on opposite faces. Typical results of these first experiments are shown in Figure 2 where the ordinate is the change in photocurrent due to the infrared. While a quenching seems to
FIG. 1 SAMPLE CONFIGURATION
Fig. 2 - APPARENT EFFECT OF IR ON PHOTOCURRENT - SAMPLE Y-2
occur at 540 μ when the light spot is within 1 mm of the contacts, these results were not reproducible and probably resulted from fluctuations in the intensity of the monochromater beam. The light source used for the monochromater was powered from the a.c. line, and even though a Sola transformer was used to regulate the line voltage, the regulation was not perfect.

The method of measurement was then changed so that the photocurrent was measured with and without infrared incident on the crystal for each wavelength before proceeding to the next monochromater setting. This procedure eliminated erratic results due to long term drift and fluctuations. These measurements were far more reproducible, and indicated that the infrared radiation caused no modulation of the photocurrent in some 25 crystals.

It is recognized that one of the factors determining the sensitivity of exciton-induced photoconductivity to quenching by infrared is certainly the rate of exciton production by visible light. In an effort to increase the rate of exciton production the incandescent lamp source for the monochromater was replaced by a mercury-xenon high pressure arc lamp, and finally the monochromater itself was replaced by a 550 μ interference filter. The center wavelength and band width of the light passed by this filter could be adjusted to shorter wavelengths by tilting the filter.

The measuring instrument in all the work thus far discussed was a Keithley 150-A Microvolt-Ammeter. In addition to being a very sensitive instrument, this meter can be used in a suppressed-zero mode; in this mode the meter applies a bucking voltage to the incoming signal so that the meter indication is the difference between the incoming signal and the bucking voltage. With the meter then operating at a higher sensitivity the minimum detectable change in signal level is about 0.01%. Despite this excellent instrumentation,
no change in signal level was ever noted upon application of the infrared energy, even with the increased illumination brought about by the changes in the optics noted above.

B. Detection Sensitivity and an A.C. Detection System

The sensitivity of the D.C. type of measurements discussed above is far greater than that used by either Diemer and his co-workers or Robinson. In terms of Specific Sensitivity, defined as

\[ S_1 = \frac{V}{JE} \left[ \frac{(R_c + R_l)^2}{4R_c R_l} \right], \]

where

- \( V \) = rms value of signal in volts
- \( J \) = rms value of radiant energy flux in watts/cm\(^2\)
- \( R_c \) = zero signal detector resistance
- \( R_l \) = load resistance
- \( E \) = bias applied across detector and load resistor in volts

we estimate our maximum sensitivity to be about 1 cm\(^2\)/watt. For comparison, the specific sensitivity of lead sulfide detectors at 25\(^\circ\)C varies from 10 to 1000 cm\(^2\)/watt while \( S_1 \) for lead selenide detectors at 25\(^\circ\)C varies from 0.2 to 2 cm\(^2\)/watt. Actually, our minimum \( S_1 \) varies somewhat from sample to sample depending on the magnitude of various noise sources, but 1 cm\(^2\)/watt is a typical figure. Thus we can report that \( S_1 \) for these specimens of CdS is at least 10 to 1000 times less than that of lead sulfide, but could be comparable to that of lead selenide at 25\(^\circ\)C. These estimates are based on thermopile measurements of the incident infrared energy, a known battery voltage and measurable load resistance. The infrared energy transmitted by the InSb filter is 320\( \mu \) watts/cm\(^2\) at the sample location, while

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that transmitted by the germanium filter is 3350\(\mu\) watts/cm\(^2\).

In an effort to increase the sensitivity of our signal detection, the incoming infrared was chopped and a harmonic wave analyzer (tuned amplifier) was used to search for a signal. The sensitivity of this arrangement surpassed that of the previous dc measurements. About 20 crystals were examined for photoconductive quenching with this ac detection system, and no response to infrared was noted in any crystal.

At this point in the program, some 49 crystals had been examined to determine whether they exhibited the desired quenching of the photoconductivity by infrared energy in the 8-12 micron band. Many of these crystals were examined by several of the techniques and arrangements described above, yet no evidence of the quenching effect has been observed. It should perhaps be noted that quenching could nearly always be observed with unfiltered light from the Nernst glower and occasionally with the germanium filter in the path of the infrared beam, but never when the indium antimonide filter was in place. This quenching is not the effect we are seeking, but rather is caused by absorption of infrared energy of wavelength less than about 1.75\(\mu\) by trapped holes, thus hastening the recombination of photoexcited electrons and holes. The utilization of this process in a detector is futile because the effect is limited to wavelengths less than 1.75\(\mu\) and the response time constant is of the order of 1 second.

C. The Search for Exciton Diffusion

In view of the fact that no quenching by long wavelength infrared was observed in any of the relatively large number of crystals described above, we decided that a new approach to the problem might be more profitable. It
will be recalled that the essence of the proposed detector is that excitons are generated by visible light and that their lifetime should be long enough so that they may diffuse a considerable distance through the crystal. The new approach is a more definitive search for crystals in which exciton processes are observable on the premise that these processes may be more observable than the quenching effect. Those crystals in which exciton processes are important to the photoconductivity should be those in which modulation of the photocurrent by long-wavelength infrared will be most likely.

In these experiments the usual line of visible light, in which the infrared is filtered out, is focussed on the crystal several millimeters from the contacts. The light is chopped and the shape of the rise curve of the photoconductivity is observed on an oscilloscope. The experimental arrangement is shown in Figure 3. The sample holder and micrometer screw adjustment for positioning the line of visible light are more clearly shown in Figure 4. In Figure 3, the visible light source is in the rectangular box at the right; the image of the filament is focussed in the plane of the chopper, and is then collimated and refocussed on the sample. A small part of the collimated beam is reflected to a phototube which supplies the trigger for the oscilloscope. The Nernst glower is contained in the black box at the left.

If only the initial part of the rise curve is observed such that the period of observation of the rise curve of the photoconductivity is much less than the carrier lifetime then, to a first approximation, we may neglect free carrier recombination. In our experiments the total observation time never exceeded 1 millisecond, while the carrier lifetime is about 15 milliseconds. The observed photocurrent in this situation can be due to several causes: 
(a) scattering of the direct illumination by multiple reflections leading to
FIG. 3  OPTICAL BENCH ARRANGEMENT FOR OBSERVING PHOTOCONDUCTIVE RISE CURVES
true absorption in the region of the electrodes, (b) exciton diffusion from the illuminated region to the contact region where the excitons may be thermally ionized to yield free carriers, and (c) absorption and re-emission of luminescent radiation leading finally to generation of carriers by re-absorption in the electrode region.

If the photoconductivity is due to (a) above the photocurrent will initially increase with time according to

$$I = \int_0^T a F \, dT = a F T$$

where $F$ is the photon flux incident on the crystal and $a$ is that fraction of the incident flux which is scattered and absorbed near the contacts. The multiplier $a$ will depend on the distance between the contacts and the incident light.

If exciton diffusion plays an important role in the long-range photoconductivity, we would expect the initial increase of the photocurrent to be described by

$$I = I(F) I(\beta) I(T)$$

where

$$I(T) = T \left(1 + e^{-T/\tau}\right) + 2\tau (e^{-T/\tau} - 1)$$

Eq. (2) assumes the photocurrent is separable into three factors. The first factor $I(F)$ depends only on the incident light flux. The second factor, $I(\beta)$,
takes into account exciton generation efficiency and the probability that excitons reach the contact region, i.e., I(β) depends on the exciton lifetime and diffusion coefficient. The third factor, I(T), indicates the functional dependence on time of the rise of the photocurrent, but contains no amplitude information; the amplitude is given by the product I(F)I(β).

The derivation of Eq. (3) will be included in the Final Report; this equation is plotted in Figure 5. It must be noted that the origin does not represent the beginning of the illumination pulse - rather it is the point experimentally determined to be the beginning of the photoconductive rise curve. The onset of photoconductivity will be delayed by the time it takes the excitons to diffuse from the illuminated region to the contact region.

The third possible mechanism, the absorption and re-emission of luminescent radiation, will exhibit a rise curve similar to that in Figure 5 (with the appropriate time constant), but there will be no delay between the beginning of the illumination pulse and the onset of photoconductivity.

Most of the 50 crystals of CdS examined for evidence of exciton transport showed only the linear rise of the photocurrent with time, suggesting that the observed currents were due to scattered light according to Eq. (1) or to luminescent re-radiation characterized by a very short lifetime. An example of this type of result is shown in Figure 6. The important feature of the curves in Figure 6 are: (a) the curves are essentially identical for all separations between the illuminated region and the contacts, and (b) the rise curves are linear. In all the work reported in this section the maximum photocurrents are independent of the separation between the illuminated region and the contacts; that is, in the case of linear curves the product aF in Eq. (1) is constant. This is accomplished by adjusting the light intensity.

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Fig. 5 - Calculated photocconductivity rise curve due to excitons.
Fig. 6 - Photoconductive rise curves for sample A-22. In the series (a) through (e) the light spot is respectively 4mm, 3mm, 2mm, 1mm, and 1/2mm from the contacts. Time increases to the left, at the rate of 100μ sec/div.
Such a procedure eliminates any non-linear saturation effects which are sometimes observed in CdS.

In contrast to the results in Figure 6 some crystals exhibited photoconductive rise curves such as are shown in Figure 7. Notice that when the illuminated region is farthest from the contacts the curve is linear, but as the illuminated region is moved closer to the contacts a marked departure from linearity occurs. Bearing in mind that this is not a saturation effect as discussed above, it is clear that there is another mechanism contributing to the photoconductivity, a mechanism which becomes more dominant as the light spot gets closer to the contacts. The disappointing feature is that the curves in Figure 7 bear little resemblance to the curve shape expected when excitons are important in the photoconductivity (Figure 5). We have not been able to explain satisfactorily why the slope of the rise curve should decrease after times of the order of 100μ sec. An hypothesis which does lead to the experimental curve shape is as follows. If the observed curve shape is actually due to two contributions, scattered light and exciton diffusion (which is quite likely), the observed curve shape can be obtained by allowing the exciton contribution to decay to zero after several lifetimes. This is merely an hypothesis, and considerable research will be required to investigate the plausibility of this hypothesis; this effort has been initiated. It should be noted that infrared radiation (8-12μ) has no apparent effect on the observed curve shapes.

It is known that the probability of exciton formation increases with decreasing temperature. In an attempt to exploit this behaviour seven crystals were examined at 77°K. The photoconductive rise curves were measured and high sensitivity dc measurements were made in the search for an effect
Fig. 7. - Photoconductive rise curves for sample A-13. In the series (a) through (e) the light spot is respectively 4mm, 3mm, 2mm, 1mm, and 1/2mm from the contacts. Time increases to the left, at 100μ sec/div.
on the photocurrent due to infrared. A general view of the experimental arrangement is shown in Figure 8.

The departure from non-linearity in the rise curves is generally more pronounced at $77^0K$, but yet the application of infrared to the sample caused no observable change in the photocurrent. The advantages in working at low temperatures when observing exciton behaviour are sufficient, however, that much future work will be done at $77^0K$ in our efforts to rediscover exciton modulation of the photocurrent.

III. FUTURE WORK

The primary aim of future efforts will, of course, continue to be the selection of semiconductor crystals in which the photoconductivity can be quenched by 8-12$\mu$ infrared radiation. The direction of the work will be oriented more closely to the study of exciton transport than in the past, however, for we now feel that only in this way can significant progress be made.

Several questions have been raised by the work described in this report. The unexplained non-linearities in the photoconductive rise curves of some crystals should be investigated further. If, as is suspected, these curves are actually due to exciton diffusion, why are their shapes so markedly different from the expected curve shape? If, as suggested above, the exciton contribution vanishes after several exciton lifetimes, what is the mechanism for attenuation of the exciton flux? And, if we are seeing exciton diffusion, why can we not modulate this current with infrared? These questions must certainly be answered before a detector of the type proposed is optimized.
FIG. 8  OPTICAL BENCH ARRANGEMENT FOR OBSERVING PHOTOCONDUCTIVE RISE CURVES AT 77°K.
To this end, the most promising crystals already studied will be re-examined in an arrangement similar to that previously used to study the rise curves. The light pulses, however, will be very short to ensure that exciton decay is not caused by the generating source. This technique should clearly display any exciton contribution to the photoconductivity. The exciton contribution will occur after the light has been turned off and the photocurrent essentially constant. This work will be done at room temperature and at lower temperatures, ranging down to 77°K.

IV. SUMMARY

The largest part of the work done on this program has been described. The effort has primarily been a search for crystals of CdS in which exciton induced photoconductivity can be quenched by infrared radiation in the band from 8μ to 12μ. Some 90 crystals have been examined, and while the quenching has not been observed, some indication of an exciton contribution to the photoconductivity has been observed in eleven crystals. We do not yet possess a detailed understanding of the photoconductive behaviour of these eleven crystals. Thus one cannot be positive that exciton processes are important in these crystals; these uncertainties provide the motivation for work in the immediate future.

The most singular feature of this work is that the desired quenching effect was never observed even though it had been observed previously by two other people, R. J. Robinson at ARF and Diemer at Philips Research Laboratory. Unfortunately, the crystals measured by Robinson were ground and sintered, and could not be re-examined. Since Robinson's crystals were originally grown in this laboratory, it may be necessary in any future work...
to grow new crystals again. This adverse development has forced a re-orientation of the program away from an Edisonian search for suitable crystals and toward a more fundamental study of exciton transport.
REFERENCES


