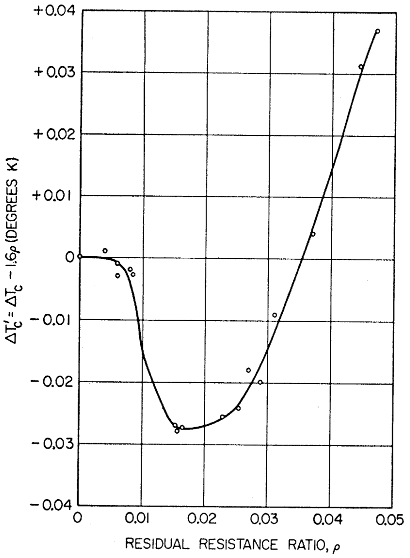

FIG. 11. The nonlinear portion of the change in critical temperature as a function of composition.

low-temperature measurements by using the BCS expression for γ. This will not give the correct answer since it is based on the assumption that the low of corresponding states is valid, but the number obtained can be easily revised when the BCS theory is improved. The various alloys, however, all have the same reduced critical field within the range of temperature over which the measurements extend. The variation of γ with composition will thus be independent of the specific formula that is used to calculate γ. Unfortunately, the measurement of critical field did not extend to low enough temperatures to allow for an accurate determination of H_0, and consequently there is considerable scatter in the plot of γ vs composition. Thus no attempt will be made to draw any conclusions from this data.

The variation in T_c with composition, while not unlike that of other dilute In alloys,[22] nevertheless cannot be described in the terms used by Lynton, Serin, and Zucker.[16] If one writes as they do, that the total change in critical temperature, $\Delta T_c = A\rho\Delta T_c'$, where ρ is the resistivity ratio and A is constant then $\Delta T_c'$ does not increase monotonically as Lynton et al., suggest. This is illustrated in Fig. 11 where $\Delta T_c'$ is as large as -0.027°K, which is an order of magnitude larger than the experimental error of the determination.

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Photovoltaic Effects in CdS Crystals*

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Photovoltages were obtained in CdS crystals using inhomogeneous excitation; that is, the excitation at one electrode was much larger than at the other electrode. Voltages in the range of 200 millivolts were obtained, with the region of high excitation always becoming positive. Two types of electrode arrangements were used. Some crystals were contacted directly with electrodes, others were insulated from the electrodes by thin Mylar sheets. In the first arrangement the photovoltages were permanent, in the second transient. The photovoltage showed only a weak dependence on intensity, and only wavelengths near or shorter than that corresponding to the absorption edge were effective. With metal electrodes the photovoltages were small. However, with jelly electrodes contacting the crystals photovoltages were almost as large as for the insulated crystals.

A. INTRODUCTION

PHOTOVOLTAGES in semiconductors normally arise at the metal-semiconductor interface or at a transition region such as an n-p junction between two differently activated sections of the semiconductor. The photovoltages to be discussed here, however, are due primarily to the inhomogeneous excitation of the samples, which produces a concentration gradient of free charges in the material. Photovoltages due to concentration gradients (Dember effect) have also been given some attention in the literature.[1]

The measurements which comprise the subject matter of the present paper were designed to dis-

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† Also with Physics Department, Hunter College, Bronx, New York.

[1] L. Bergmann and F. Ronge, Physik. Z. **41**, 349 (1940); L. Bergmann, *ibid.* **33**, 209 (1932); H. Dember, *ibid.* **32**, 554 (1931); **32**, 856 (1931).

criminate between the different effects which contribute to the production of a photovoltage, namely, the effect of the electrodes, and the effect of the concentration gradient. Therefore two different lines of investigation were pursued. In the first, electrode contacts were made directly to CdS crystals with electrode jelly, silver paste, and indium. In the second, in order to eliminate the influence of the electrodes, the surfaces of the crystals were coated with thin sheets of transparent insulating material with a semitransparent aluminum backing.

B. EXPERIMENTAL PROCEDURE AND RESULTS

1. CdS Crystals with Electrode Contacts

Table I lists results obtained with five CdS crystals with electrode contacts. All except *S*-44 were grown by the Eagle Picher Research Laboratories using a method which is an adaptation of that first reported by Czyzak *et al.*[2] This was the sublimation of CdS in a neutral atmosphere over a period of approximately 100 hours with crystal deposition occurring on a polished quartz substrate maintained at a slightly lower temperature then the volatilizing charge. Crystal *S*-44 was grown from the vapor phase at 900°C according to the method of Frerichs and Warminsky[3,4] and copper activated with CuCl, both growth and activation having been carried out by the Hupp Corporation. The electrodes were Cambridge Electrode Jelly. The choice of this particular material was suggested by the observation that water electrodes behave differently from metal electrodes in that they seem to facilitate the exchange of positive holes.[5] Jelly was found to have the same properties as water and was much easier to work with. The electrodes were applied to the two ends of the long dimension of the crystal for those crystals listed in Table I. [Some flat thin crystals similar to those used with insulated electrodes (Sec. 2) had the jelly electrodes placed on opposite surfaces with the thin dimension between them, so that there were clearly bulk rather than surface effects when the flat sides were illuminated. These crystals gave results similar to those which had the electrodes at the ends.] Voltages were measured with a Keithley electrometer No. 220 with infinite input resistance. The short circuit current was measured with a Leeds & Northrup galvanometer, Model 2430-D.

In each case there was a marked increase in voltage when only half the crystal was illuminated compared to the voltage obtained when either the entire crystal was illuminated, or when there was no illumination at all. Approximately the same photovoltage, but of opposite polarity, was obtained when the other half of the crystal was illuminated. With no illumination a residual, slowly decaying, voltage was observed which overnight reached the value in the table. The small voltage obtained under full illumination or in the dark is probably due to some asymmetry either in the crystal or at the electrodes.

TABLE I. Photovoltages of several electrode contacted CdS crystals under various conditions of illumination.

	Illumination[a]	Open circuit voltage in volts[b]	Short circuit current in units of 10^{-10} amp
Crystal	Dark	0.004 to 0.008	...
S-44	Fully illum. (vis.)	0.044	202
	Fully illum. (uv)	0.030	294
(2.0 cm ×0.1 cm ×0.05 cm)	Half illum. (vis.)	0.210	111
	Half illum. (vis.) *ND*1	0.190	24.5
	Half illum. (vis.) *ND*2	0.165	3.5
	Half illum. (vis.) *ND*3	0.09	0
	Half illum. (vis.) +fully illum. (uv) on other side	0.050	81
Crystal	Dark	0.006 to 0.030	...
S-43	Fully illum. (vis.)	0.011 to 0.024	...
	Fully illum. (uv)	0.005 to 0.064	0
(2.5 cm ×1.0 cm ×0.25 cm)	Half illum. (vis.)	0.230	91
	Half illum. (vis.) *ND*1	0.240	15
	Half illum. (vis.) *ND*2	0.160	3.5
	Half illum. (vis.) *ND*3	0.073	...
	Half illum. (vis.) *ND*4	0.045	...
	Half illum. (vis.) +full illum. (uv) on other side	0.110	67
Crystal	Dark	0.002 to 0.007	...
S-42	Fully illum. (vis.)	0.032	...
	Half illum. (vis.)	0.150	115
(3.0 cm ×0.6 cm ×0.25 cm)	Half illum. (vis.)		
	+2–64 Corning filter (λ >6500)	0.028	...
	+2–60 Corning filter (λ >6100)	0.032	...
	+2–62 Corning filter (λ >5900)	0.042	...
	+3–66 Corning filter (λ >5600)	0.058	...
	+3–67 Corning filter (λ >5400)	0.070	...
	+3–68 Corning filter (λ >5300)	0.085	...
	+3–72 Corning filter (λ >4400)	0.145	...
Crystal	Dark	0.024 to 0.045	...
S-41	Fully illum. (vis.)	0.014	7
	Half illum. (vis.)	0.225	88
(3.0 cm ×0.6 cm ×0.3 cm)			
Crystal	Dark	0.001	...
S-40	Fully illum. (vis.)	0.020	38
	Half illum. (vis.)	0.183	84
(2.0 cm ×0.3 cm ×0.5 cm)			

[a] Visible—tungsten illumination—5.7 milliwatts/cm^2 total uv—1 milliwatt/cm^2 primarily at 3600 A.

[b] The polarity in the dark or under full illumination varies, but under half illumination the illuminated side is always positive.

To investigate the dependence of photovoltage on intensity, a series of Wratten neutral density filters were used. Although these filters doe not attenuate properly at wavelengths longer than 7000 A, it was of little consequence in these measurements, since the absorption of CdS crystals in this region is very low. In the two cases where the intensity was investigated, in crystals *S*-43 and *S*-44, there was only a small decrease in voltage with large decreases in intensity. For instance, with *S*-44, when the intensity was reduced by a factor of 100, the voltage decreased by only 21%. The short circuit current, however, was considerably lower at this intensity, 3% of the value at the highest intensity. With *S*-43, the results were similar. The voltage was reduced by 30% when the intensity was

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[2] Czyzak, Craig, McCain, and Reynolds, J. Appl. Phys. **23**, 932 (1952).

[3] R. Frerichs, Naturwissenschaften **33**, 281 (1946).

[4] R. Warminsky, Ph.D. thesis, Technical University of Berlin, 1948 (unpublished).

[5] Daniel, Schwarz, Lasser, and Hershinger, Phys. Rev. **111**, 1240 (1958).

TABLE II. Photovoltages of several insulated CdS crystals under various conditions of illumination.

Crystal	Illumination (Side *A*)	Illumination (Side *B*)	Photovoltage peak (Polarity of *A* with respect to *B*)
G-1	Blue light[a]	None	+0.100*V*
	Blue light+31.5% filter	None	75% of value without filter
	Blue light+6.5% filter	None	42% of value without filter
	Blue light+0.6% filter	None	8% of value without filter
	Tungsten source+Corning 2–64 ($\lambda>6500$)	None	Fluctuating between −0.010 and +0.050*V*
	Tungsten source+Corning 7–56 ($\lambda>8000$)	None	0
G-2	Blue light	None	+0.135*V*
	Blue light+31.5% filter	None	95% of value without filter
	Blue light+6.5% filter	None	84% of value without filter
	Blue light+0.6% filter	None	50% of value without filter
	Tungsten source+Corning 2–64 filter ($\lambda>6500$)	None	Fluctuating between −0.015 and +0.010*V*
	None	Blue light	−0.135*V*
	None	Tungsten source+Corning 7–56 ($\lambda>8000$)	+0.010*V*
	Blue light	Tungsten source+Corning 3–68 ($\lambda>5300$)	+0.060*V*
	Blue light	Tungsten source+1–56 ($4000<\lambda<7000$)	+0.060*V*
	Blue light	Tungsten source+Corning 2–64 ($\lambda>6500$)	+0.100*V*
	Blue light	Tungsten source+Corning 7–56 ($\lambda>8000$)	+0.200*V*
S-1	Blue light	None	+0.170*V*
	Tungsten source+Corning 2–64 ($\lambda>6500$)	None	+0.010*V*
	None	Blue light	−0.160*V*
	None	Tungsten source+Corning 2–64 ($\lambda>6500$)	+0.020*V*
S-2	Blue light	None	+0.140*V*
	Tungsten source+Corning 2–64 ($\lambda>6500$)	None	Fluctuating between −0.030 and +0.020*V*
	None	Blue light	−0.160*V*
	None	Tungsten source+Corning 2–64 ($\lambda>6500$)	Fluctuating between −0.020 and +0.020

[a] 50 watt tungsten source with $CuSO_4$ solution and Corning 5–61 filter, 6μ watts/cm^2 passing through mylar with $\lambda<5200$ A.

decreased by a factor of 100, while the current was more markedly reduced.

The spectral response of crystal *S*-42 was obtained using a series of Corning glass filters with different cutoffs. The photovoltage increased as the wavelength region extended to shorter wavelengths. For Corning filter 2–64 ($\lambda>6500$) only 0.028 volt was obtained, but for Corning filter 3–72 ($\lambda>4400$) the photovoltage was almost as great as when no filters were interposed. Thus, only wavelengths near or on the short side of the absorption edge are effective, since the other wavelengths are absorbed only weakly. This is quite different from Reynold's results,[6] where appreciable photovoltages were also observed in the 6000 A to 8000 A region.

The addition of excitation to the other side of the crystal over that entire surface decreased the photovoltage, as can be seen from the last lines in Table I for crystals *S*-44 and *S*-43. This effect was observed whether the second side was illuminated with uv or with visible light. uv excitation on only half the crystal gave photovoltages of approximately the same magnitude as when visible excitation was applied to the same half.

When metal electrodes (indium or silver paste) were used instead of the jelly electrodes, the photovoltages were markedly reduced, and the results were not as constant, although the polarity effect (irradiated portion positive) still obtained.

2. Insulated CdS Crystals

These flat, thin crystals were grown in the same manner as crystal *S*-44. They were sandwiched between sheets of Mylar 0.001 cm thick, which were backed with a commercially deposited, semitransparent, aluminum layer. The aluminum coated Mylar transmitted about 5% of the incident light in the visible and near infrared regions of the spectrum; with no filters between the source and crystal about 500 μwatts/cm^2 passed through the Mylar and were incident on the face of the crystal, as measured by a thermopile.

The impedance changes as a function of illumination

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[6] Reynolds, Leies, Antes, and Marburger, Phys. Rev. **96**, 533 (1954).

of these crystals had been studied previously.[7] In the series of measurements described here only the photovoltaic effect was investigated, using an electrometer tube as a high impedance converter between the sample and an oscilloscope.

The photovoltages obtained were always transient because the final voltage appears across the Mylar insulator. Temporarily, part of the voltage appears across the electrometer grid resistance, which discharges at a rate determined by that resistance and the input capacitance. With high grid resistances the decay of the voltage at the scope was much slower than the change in photovoltage at the crystal. The crystals were illuminated until the voltage at the electrometer had decayed. The voltages observed on the oscilloscope usually reached a maximum shortly ($<\frac{1}{10}$ sec) after the beginning of illumination. The peak heights of the voltage pulses obtained under various conditions of illumination are given in Table II. As will be shown below, the actual photovoltage produced in the crystal was about twice this value. Just as was the case with the electrode contacted CdS crystals the excited side always showed a positive polarity. The inhomogeneous excitation in this case arose from the use of strongly absorbed radiation ($\lambda < 5100$ A) which produced a large number of free charges only at the illuminated side of the crystal. When light of wavelength greater than that corresponding to the absorption edge was used, so that both sides of the crystal were uniformly illuminated, the photovoltage was greatly reduced and the polarity was no longer dependent upon the direction of illumination but rather to assymetries in the crystals.

Using blue light with crystals *G*-1 and *G*-2 the dependence of the photovoltage on intensity was rather small; even when the intensity was reduced to 0.6%, the peak was reduced to 8% for *G*-1 and 50% for *G*-2.

The addition of illumination to the side opposite the side irradiated with blue light led to some interesting effects. When the "nonblue" side was irradiated with wavelengths that cause excitation, the photovoltage peak was reduced, but when infrared radiation was used on this side, the photovoltage peak was increased. Although results for only four crystals are given in Table II, preliminary measurements on four additional CdS crystals produced by Eagle Picher duplicated the results reported here. The infrared enhancement effect, however, was lacking in two crystals, indicating that for these two crystals the infrared caused some excitation.

C. DISCUSSION

1. Insulated Crystals

We will consider first the case of the insulated crystals, since this seems to be the simpler one. If a photovoltage, V_{ph}, is developed across the crystal, then a voltage V_{el} appears at the input of the electrometer, which is given by $V_{\text{el}} = V_{\text{ph}}[1 - C_{\text{el}}/(C_{\text{el}} + C_{\text{my}})]$ where C_{el} is the capacitance of the electrometer and C_{my} is the capacitance of the two Mylar sheets in series. With the Mylar capacitance roughly equal to C_{el} one obtains $V_{\text{el}} \sim V_{\text{ph}}/2$. This voltage appears at the electrometer when the time constant of the electrometer is long compared to the time the photovoltage requires to be established. Photographs of the photovoltage appearing at the oscilloscope show that this latter condition was fulfilled.

We assume that the photovoltage in the insulated case is only a diffusion voltage, which comes about by the movement of the more mobile charges into the less excited region. Since in CdS the positive holes have a very small mobility, one can carry out the calculation as if only the electrons diffuse, and obtain in this manner $V_{\text{ph}} = (kT/e) \ln(n_l/n_d)$, where n_l and n_d are the densities of free electrons in the excited and unexcited regions, respectively. (The effect of trapping enters this equation only through the concentration ratio of free carriers. If, however, the traps are not saturated, this ratio is independent of the number of traps.) The ratio n_l/n_d can be obtained from photoconductivity data. When one estimates that under the given illumination this ratio is of the order of 10^4, a photovoltage of about 150 millivolts is obtained. This value corresponds closely to the experimental results.

It might be of interest to consider the effect of the possibility that the surface layers have properties different from those of the bulk material. If, for instance, at the illuminated surface particularly strong recombination would occur, this would result in a decrease in photovoltage, since the concentration of free electrons at the illuminated side would decrease.

The experiments show the typical weak dependence of photovoltage upon intensity of illumination. See the results for crystal *G*-2 in Table II, for example. This is due to the ln term in the equation for V_{ph}. The experiments with illumination on both sides of the crystal give credence to the idea that there is a diffusion voltage which depends upon the ratio of the densities of excited electrons at the surfaces. With visible light applied simultaneously with blue light but on the side opposite to the blue illumination the V_{ph} is decreased, because at the "nonblue" side n_d is increased. However, with quenching light on this side the V_{ph} is increased, probably because the ratio n_l/n_d is increased by the quenching radiation. This might appear strange at first sight, since the quenching radiation penetrates the entire crystal, but one must consider that the degree of quenching of strong excitation is much smaller than that of weak excitation.[8] In the excited region the quenching may amount to a factor of 2 or 3, while in the unexcited region it is much larger. This is apparently

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[7] H. Kallmann, B. Kramer, and G. M. Spruch, Phys. Rev. **116**, 628 (1959).

[8] H. Kallman and B. Kramer, Phys. Rev. **87**, 91 (1952).

responsible for the increase in photovoltage from 0.135 to 0.200 volt in crystal *G*-2.

The experiments indicate that quenching on one side of the crystal influences the photovoltage. It would seem that the converse might also be true, namely, if a crystal which exhibits different recombination rates in different sections is uniformly excited, a photovoltage will develop.

2. Crystals with Electrodes

The experiments with electrodes applied to the crystals can be interpreted in a similar way except that the change at the electrodes brought about by the illumination must be taken into account together with the diffusion voltage. This voltage change cancels the diffusion voltage exactly if the Maxwell-Boltzmann distribution prevails and if only one carrier type is active. The first condition was pointed out by Landau and Lifshitz.[9] If both positive holes and electrons participate in the conductivity phenomenon there is a particle current flowing into the electrode, but the electric current is zero (open circuit voltage measurement) so that the flow of electrons and the flow of holes are equal. Because of the particle current the concentration near the electrodes changes, as does the potential gradient, and the Maxwell-Boltzmann distribution is no longer valid. The voltage is dependent upon the mobility of the two carriers; therefore it is not necessary that the diffusion voltage compensate the voltage change at the electrodes.

The fact that the illuminated electrode is always positive as was the case with insulated crystals, and that the observed photovoltages are of the order of 0.2 volt, slightly smaller than those observed for the insulated crystals although the exciting intensity was larger, certainly indicates that the diffusion voltage is not fully compensated by the change in potential near the electrode. Apparently a positive charging of the illuminated electrode takes place which prevents a larger change in electrode potential. Since appreciable photovoltages occurred only with jelly electrodes and not with the indium or silver paste electrodes, we conclude that the jelly electrodes in some way favor the exchange of positive holes with the electrodes.

The photovoltages for full illumination were small in crystal *S*-44 (this is to be expected since then the situation is the same at both electrodes and no concentration gradient exists). It was observed, however, that in spite of the small photovoltage there was a large current. This is probably due to the small photovoltage developed with uniform excitation when there is a small accidental difference between the two electrodes, combined with the relatively low total resistance under full illumination. One could also interpret this current as having been produced purely by an electrochemical voltage between the two electrodes, which shows up more strongly under illumination because of the higher conductivity, while without illumination this small voltage cannot produce such currents. In the case of the half illuminated sample this purely chemical interpretation is impossible because the sign of the voltage is determined by the illumination. Here the large voltages occur because of the nonuniformity of the illumination.

The slow change of voltage with intensity of excitation is typical of photovoltages brought about by a concentration gradient in a single cell.

The drop in voltage with increasing wavelength means that absorption in the valence band is by far the predominant factor in producing photovoltages. A comparison of the results obtained for various wavelengths with those obtained for different neutral density filters makes this quite evident. Cutting out the wavelength range between 4400 A and 5400 A caused the photovoltage to decrease to 0.085 volt. An *ND* 2 filter (10^{-2} transmission) made the photovoltage drop from 0.230 to 0.160 volt. Therefore the drop to 0.085 volt caused by cutting out the above wavelength range is equivalent to an intensity drop of more than a factor of 100.

Finally, it may be of interest to discuss the question of how to increase the power output of these crystals. The low power output is due to the relatively high resistance of the nonilluminated side, which is of the order of 2×10^7 ohms. Probably the entire photovoltage lies across this nonilluminated part of the crystal in the short circuit experiments. To reduce the resistance, experiments were performed in which the crystals were half illuminated on one side and fully illuminated on the other side with a different wavelength. It was hoped that this would reduce the resistance without influencing the photovoltage. Apparently the latter is not the case, however. The full illumination reduced the photovoltage as well as the resistance, because the asymmetry between the two sides of the crystal was also reduced. But it is worth noting that the current was reduced less than the photovoltage was; certainly this was due to a reduction in resistance.

Another means of reducing the resistance and increasing the power output would be to raise the dark conductivity of the sample by introducing impurities. This must be done in such a way as to increase the number of free electrons. But such an increase would influence the photovoltage.

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[9] L. Landau and E. Lifshitz, Physik. Z. Sowjetunion **9**, 477 (1936).