of such density that a drop added to the calibrating solution represented a stepwise change of about 5×10^{-6} g/cc. Considerable time is necessary to determine the influence of each final drop since the solution must be free of currents and temperature equilibrium must be assured.

The density of the solution found just sufficient to float a calibration sphere was determined in a volumenometer pycnometer calibrated with boiled distilled water.[11] The calibration is good to ±0.00001 g/cc, based on a consideration of the measurement errors.

The liquids used to measure density were made from two solutions, one of which would just float, and the other of which would just sink the calibration spheres. After a column had been prepared, it was possible to have two calibration spheres whose density differed by 310×10^{-6} g/cc separated by about 10 cm in the column. The position of the specimens in the column was read on a cathetometer to ±0.1 mm. The sensitivity of the method was therefore of the order 3×10^{-7} g/cc even though the densities are known on an absolute scale to only 10^{-5} g/cc.

It was found convenient to have the silicon samples in the form of spheres. Spheres 3 to 4 mm diameter were prepared by tumbling polyhedra of silicon over silicon carbide paper in a circular "race-track." The polyhedra were propelled by introducing a stream of air tangentially to the circular track. The spheres were etched bright and smooth in 3 HNO_3, 1 HF, washed in distilled water, treated in HF, and again rinsed in distilled water. This treatment had been found by Gallagher and Blodgett to give a hydrophobic surface.[12] Successive treatments did not alter the density as determined from the position of flotation in a density column.

Although much effort is required to set up and calibrate a density column, once prepared the columns may be used for months. Samples may be removed and added using a platinum screen cup on the end of a wire. Care is necessary to avoid excessive agitation and time must be allowed for equilibration before dependable measurements may be made. Without sample changes, a column appears to lose less than 5 percent sensitivity in a month.

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[11] N. E. Dorsey, *Properties of Ordinary Water* (Reinhold Publishers, New York, 1940), p. 200.

[12] G. J. Gallagher and K. B. Blodgett (private communication).

PHYSICAL REVIEW VOLUME 97, NUMBER 6 MARCH 15, 1955

Properties of Ohmic Contacts to Cadmium Sulfide Single Crystals

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(Received September 21, 1954)

The usual materials and techniques for making electrical contact to CdS single crystals are not satisfactory. The *V–I* characteristics are erratic and nonlinear, the photocurrent noise is excessive and there is a spurious photovoltaic effect, all associated with poor, high-resistance contacts. It has been found that In and Ga make ohmic contact to the crystals. With ohmic contacts the disturbing effects of the barriers are removed and measurements of the electrical characteristics of the crystals can be made with confidence. In addition, maximum performance can be obtained from the crystals. From the measurements it is shown that there can be large volume photosensitivity in CdS, and that the surface and volume (dark) conductivity of a crystal can differ greatly. Typical *V–I* characteristics are presented demonstrating: (1) The improved performance obtained from a photosensitive CdS crystal with In contacts compared with that obtained with the Au contacts; (2) broad-area CdS crystal rectifiers. One was made from highly conducting crystals from which a forward current density ~1 amp/cm² was obtained at 1.5 volts with a front to back current ratio of 10^6. The other, a rectifier-photoconductive cell, was made from an insulating photosensitive crystal. In the forward direction the gain was $>10^4$ at 6 volts (corresponding to ~10 amp/lumen). (3) Space-charge-limited current in an insulator. The current is time dependent and increases more rapidly with voltage than the square-law theoretically predicted for a perfect insulator. The effect of crystal imperfections in determining the *V–I* characteristics is indicated.

I. INTRODUCTION

THE availability of excellent single crystals of cadmium sulfide with controlled characteristics and the ability to make both *ohmic* and rectifying contact to the crystals[1] makes possible, from relatively simple current-voltage measurements, a determination of some of the pertinent electrical characteristics of the crystals. In addition, ohmic, rectifying, and space-charge-limited types of behavior are demonstrated. Large space-charge-limited currents in an insulator were predicted some 15 years ago by Mott and Gurney,[2] but had not been observed because the two rather critical requirements, of (1) ohmic contacts to (2) a relatively perfect insulator, had not been met. It has been shown that[3] even in the case of CdS, the theoretical square-law dependence of space-charge current on voltage is altered by imperfections in the crystal.

The contrast between measurements made with poor electrical contacts and measurements made with ohmic

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[1] R. W. Smith and A. Rose, Phys. Rev. **92**, 857 (1953).

[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), pp. 168–173.

[3] A. Rose and R. W. Smith, Phys. Rev. **92**, 857 (1953).

contacts emphasizes the importance of the electrode problem in measurements on semiconductors and insulators. Commonly used materials (Ag, Au, Cu, graphite, Pt, $\cdots$) and techniques do not make good electrical contact to CdS crystals.[4] With these electrodes the V–I characteristic is erratic and nonlinear, the potential distribution is not uniform along the crystal, the photocurrent is excessively noisy, and there is an extraneous photovoltaic effect, all characteristic of high-resistance contacts. Because of the barriers the measurements are uncertain and the performance of the crystal is limited. It has been found, however, that indium (In) and gallium (Ga) do make ohmic, noise-free contact[5] to CdS crystals. With ohmic contacts the uncertainties in the earlier measurements have been removed and in addition maximum performance can be obtained from the crystals. The following criteria are used for maximum performance for the crystal and the degree to which they are approached may be taken as a measure of the perfection of the contacts: (1) linear current-voltage characteristic, particularly at low voltages; (2) absence of photovoltaic effect; (3) maximum performance of the crystal as a photoconductor; (4) the noise associated with the photocurrent is limited only by the noise associated with the photon stream; (5) the current passed by an insulating crystal is limited by the space-charge in the crystal and not by the supply of carriers available at the electrodes. From the V–I characteristics described in this paper it is seen that the above criteria are closely satisfied and that In and Ga do make excellent ohmic contact to CdS crystals.

II. DESCRIPTION OF THE CRYSTALS

1. Crystal Preparation

The crystals used in this study were grown and treated by R. H. Bube, C. J. Busanovich, and S. M. Thomsen of these Laboratories. They were grown by the vapor phase technique.[6,7] If pure Cd and pure H_2S are used, insulating crystals are obtained. In practice it seems easier to grow conducting crystals by the addition of halogen to the reacting vapors and to subsequently treat the resulting crystals by controlled impurity additions, usually Ag or Cu.[7]

2. Physical Characteristics

CdS crystals are normally *n*-type. Many tests have been made for hole conduction with generally negative results. The crystal resistivity can be controlled from ~ 1 to $>10^{13}$ ohm-cm. The resistivity obtained for a particular crystal can depend on the way it is measured; if for example, the measurement is made between two electrodes on the same side of the crystal an apparent (surface) resistivity of the order of 10^9 ohm-cm may be obtained. If, however, the measurement is made with electrodes on opposite faces of the crystal a (volume) resistivity of the order of 10^{12} ohm-cm may be obtained. An upper limit to the electron mobility seems to be ~ 200 cm^2/volt-sec. The energy gap between the filled band and the conduction band is 2.4 ev and there is ample evidence for traps distributed in the "forbidden" band.[8] For highly conducting crystals the current ratio, ΔI (photocurrent) : I (dark) is less than unity. As the resistivity is increased, by impurity additions, the ratio increases to values as high as 10^8 for ρ of the order of 10^9 ohm-cm. The purer crystals are more insulating and rather insensitive photoconductors.

The size and shape of the crystals depend critically on the growing conditions. The crystals used in this study were usually thin clear plates. The structure and degree of crystal perfection has been determined by J. Amick and G. Neighbor of these Laboratories and from their x-ray measurements the crystals appear to be excellent single crystals of the hexagonal form.

III. ELECTRODES FOR CdS CRYSTALS

1. The Rectifying Contact

There is normally no problem in making rectifying contact to CdS crystals. In fact, the problem in the past was how to make ohmic contact. There are, however, several applications where good rectifying contacts are needed. Air-drying Ag paste is easy to apply, and produces an excellent rectifying contact. Evaporated Au is good as a semitransparent electrode for a rectifier-photoconductive cell. As a guide it may be said that a high work function metal makes a good rectifying contact to CdS crystals.

2. The Ohmic Contact

Indium and gallium appear to be exceptional in that they do make noise-free, ohmic contact to CdS crystals. There is little difference in performance between the two elements. In (mp 155°C) and Ga (mp 29.8°C, usually a liquid at room temperature) are metals that are relatively stable in air. There is no apparent reaction of In or Ga with CdS and diffusion into the crystal is not necessary for an ohmic contact. In fact, simple pressure contact to the crystal has given ohmic characteristics. A simple and convenient technique of applying electrodes is to evaporate an opaque layer of In on the crystal.

IV. THE CURRENT-VOLTAGE CHARACTERISTICS

1. The Linear V-I Characteristic

Figure 1 contrasts typical V–I characteristics for two similar, photosensitive crystals with different electrodes. The electrode separation and irradiation is also similar. Figure 1(a) is the characteristic with Au elec-

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[4] R. W. Smith, RCA Rev. **12**, 350 (1951).

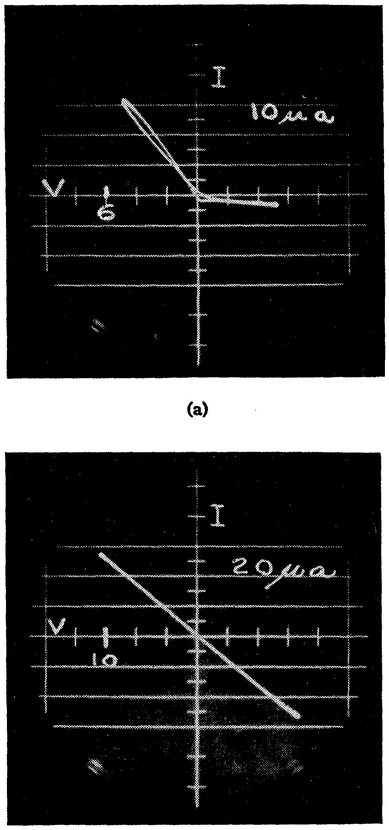
[5] Shulman, Rose, and Smith, Phys. Rev. **92**, 857 (1953); C. I. Shulman, Phys. Rev. (to be published).

[6] R. Frerichs, Phys. Rev. **72**, 594 (1947).

[7] R. H. Bube and S. M. Thomsen, J. Chem. Phys. **23**, 15 (1955).

[8] R. H. Bube, J. Chem. Phys. **23**, 18 (1955).

trodes. The nonlinearity is obvious, the potential distribution along the crystal is not uniform, the photocurrent noise is excessive and there is a photovoltaic effect. Figure 1(b) is the characteristic with In electrodes. The curve is linear from low voltages up to the point where heating effects become important and is linear for a large range of light levels. Shulman[5] has measured the photocurrent noise and found that at the lower limit it can be determined by the noise of the absorbed photon stream. The photovoltaic effect can be negligibly small. When measured under high light conditions, maximum photoconductive performance[9,10] is obtained from the CdS crystal.



(a)

(b)

FIG. 1. Oscilloscope traces of V–I characteristics of similar insulating, photosensitive CdS crystals. (a) Typical nonlinear trace obtained with the usual electrode materials, in this case Au. (b) Linear characteristics obtained with In electrode.

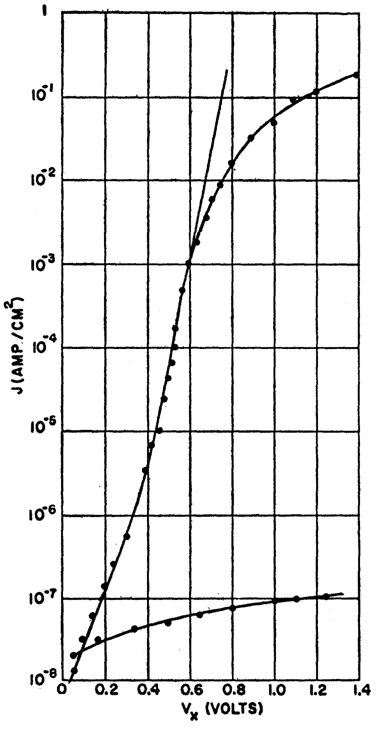


FIG. 2. Broad-area CdS crystal rectifier. One Ag and one In electrode on conducting CdS crystal.

The curves of Fig. 1 were taken with low voltages across the crystal where the nonohmic character of poor contacts is emphasized. At higher voltages, the curve in Fig. 1(a) becomes more nearly linear and it was under these conditions that the expression (1) for the gain, θ, was originally[4] verified for CdS.

With electrodes widely separated on the surface of the crystal it is difficult to determine whether the photoconduction is a surface or volume effect. One way of separating the two effects is to arrange the electrodes opposite one another on the thin section of the crystal and irradiate only the electrode area with light that can penetrate the crystal. If the gain expression (1) is satisfied, and if the gain is comparable to that obtained with the other electrode arrangement, a large volume photosensitivity is thereby demonstrated. For this test through the crystal lower voltages are used because the electrode separation is smaller. With Ag, Au, $\cdots$ (nonohmic) contacts the disturbing effect of the barriers at the contacts introduced uncertainties in the application of (1). With In or Ga ohmic contacts, the barriers are not present and the volume photoconductivity can be determined with confidence. The measurement has been made and there is a large volume photoconductivity in CdS. This has also been verified by measurements in the forward direction on a CdS crystal photoconductive rectifier to be presently described.

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[9] The performance of a photoconductor[4,10] can be evaluated as follows: With a high level of light on the crystal, the effect of traps is minimized and the observed time constant, τ_0, approaches the life time, τ, of the free carriers. If under these conditions the experimentally determined quantities satisfy the expression for the gain, θ:

$$\theta = I/eF = \tau_0 \mu V/L^2, \tag{1}$$

maximum performance is obtained from the photoconductor. The measured quantities are the photocurrent I (amp) for F absorbed photons per sec with V(volts) across electrodes L(cm) apart. The mobility $\mu \sim 100$ cm^2/volt-sec for CdS and e is the electronic charge.

[10] A. Rose, RCA Rev. **12**, 362 (1951).

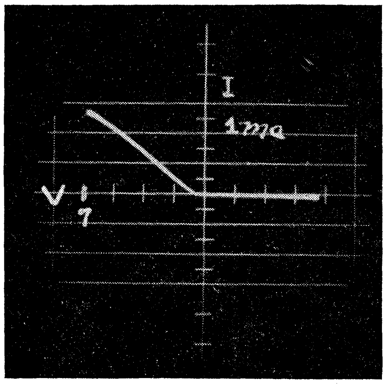

FIG. 3. Oscilloscope trace of *V–I* characteristic of broad area rectifier-photoconductive cell. Semitransparent Au electrode and opaque In electrode on insulating photosensitive CdS crystal. Room irradiation.

2. The Rectifier Characteristics

The CdS crystal rectifier is made with two dissimilar electrodes on the crystal, one an ohmic contact made with In, the other a rectifying contact made with Ag or Au. The rectifiers are broad area devices (limited only by the crystal dimensions) in contrast with the point contact rectifiers that are readily made with two similar metals. Two types of CdS rectifiers have been made, one from highly conducting crystals, and the other from more insulating crystals for which the photocurrent can be many orders of magnitude greater that the dark current.

A. The Conducting Crystal Rectifier

Figure 2 shows the dc characteristic of a conducting ($\rho \sim 10$ ohm-cm) CdS crystal with a Ag rectifying contact. The current density in the forward direction at 1.5 volts is approximately 1 amp/cm^2 and the forward to back current ratio is greater than 10^6. The forward direction is with the Ag positive, consistent with *n*-type CdS. A photovoltaic effect of a few tenths of a volt has been measured.

B. The Rectifier Photoconductive Cell

The broad area rectifier-photoconductive device is made with an In electrode on one side of a thin ($\sim 5 \times 10^{-3}$ cm), insulating, photosensitive crystal and a semitransparent Au rectifying contact on the other side. The cell is normally operated in the forward direction, Au positive. Figure 3 shows the *V–I* characteristic for a cell irradiated with room light.

Under high light conditions and operated in the forward direction with 6 volts across the crystal, the observed time constant τ_0 was 2×10^{-3} sec and a gain, $\theta > 10^4$ (corresponding to ~ 10 amp/lumen), was measured with both uniform irradiation and with a small spot of green light. Maximum theoretical performance of the photoconductor was obtained with the small spot of green light. Since the electrode spacing used in computing this performance was the crystal thickness, this is unambiguous evidence that the currents were volume currents and that high photosensitivity can be obtained as a pure volume effect without recourse to any special properties of the surface.

3. Space-Charge-Limited Current

A perfect insulator with ohmic contacts should be able to pass an appreciable current. The expression derived by Mott and Gurney for the space-charge-current in an insulator is

$$J = 10^{-13} \mu k V^2 / L^3, \qquad (2)$$

where J (amp/cm^2) is the current density between plane parallel electrodes with V (volts) across L (cm). The drift mobility μ is 100 cm^2/volt-sec and the dielectric constant k is 10, for CdS. For a typical CdS crystal, L is 5×10^{-3} cm, and the electrode area is 10^{-2} cm^2. The space-charge current expected from the square-law (2) is 1 ma for $V = 35$ volts. By contrast the ohms law current, assuming $\rho = 10^{12}$ ohm-cm, would be 10^{-11} amp for the same voltage. For CdS crystals, currents far in excess of the Ohm's law value are measured and in fact under certain conditions the theoretical square-law has been verified.[11]

Figure 4 shows the dynamic *V–I* characteristic, as seen on an oscilloscope, when a 60-cps sine voltage is applied between In electrodes opposite one another on the thin section of an insulating CdS crystal. Linear photocurrent curves are obtained with light on the crystal (F_1 and F_2 represent two different light levels).

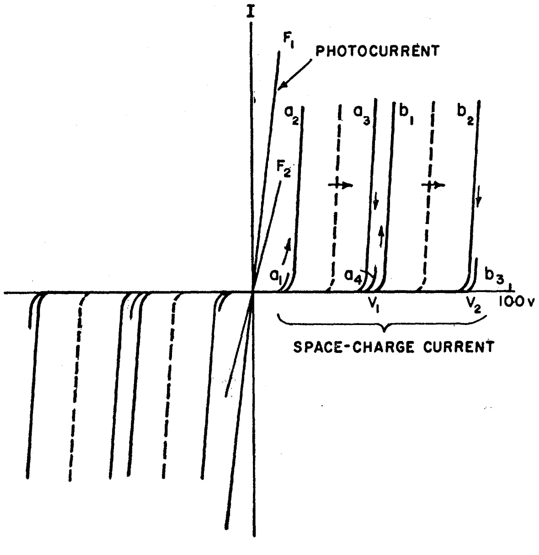

FIG. 4. Space-charge current in an insulator. Sketch illustrating *V–I* characteristics, as seen on an oscilloscope, of insulating CdS crystal with In electrodes opposite one another on the thin section of the crystal. 60-cps voltage applied across crystal.

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[11] R. W. Smith and A. Rose, following paper [Phys. Rev. **97** 1531 (1955)].

If now the crystal is placed in the dark and the voltage amplitude (V) slowly increased, the curve a_2 is traced out. With continued increase of V, the trace moves away from the I-axis to a_3. If, when the trace reaches a_3, the voltage amplitude is held fixed at V_1, the trace gradually falls to a_4. If now V is turned to zero and again slowly increased, no trace is obtained until V reaches V_1 and then b_1 is traced out and moves away from the I-axis toward b_2 with further increase in V. If V is reduced to zero, the crystal exposed to light, and then again placed in the dark, a similar sequence of curves is again obtained as V is changed.

Figure 5 represents dc measurements on a similar crystal. For each increase in voltage there is a high transient current that slowly approaches a lower stationary value. In the dark this is represented by the curve I_0. This is the steady space-charge current that can be passed by insulating CdS. If the crystal is irradiated with different light levels L_1, L_2, and L_3, linear photocurrent curves are obtained from low voltages up to the point where the I_0 characteristic predominates.

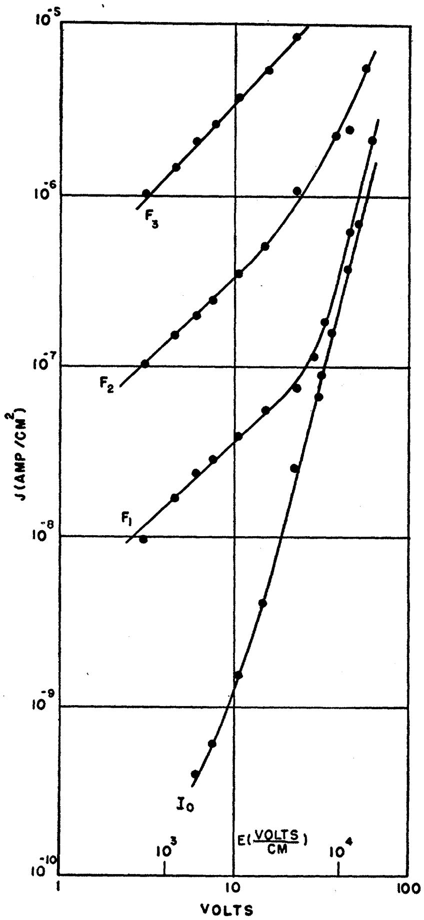

FIG. 5. Space-charge-limited current in an insulator. Dc measurement on crystal similar to that of Fig. 4. I_0 is dark current curve and F_1, F_2 and F_3 are curves with increasing irradiation.

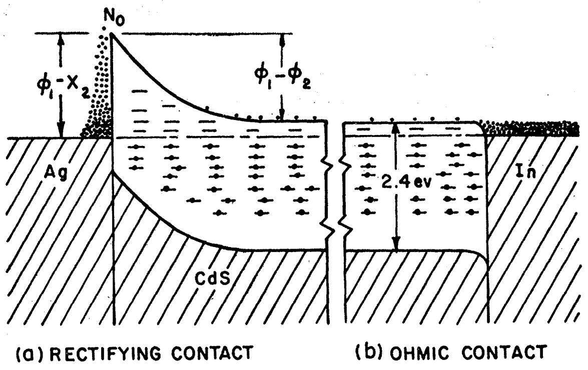

FIG. 6. The contact between a metal and semiconductor. (a) Rectifying barrier obtained with high work function metals. (b) Ohmic contact. The density of carriers, N_0, available to the semiconductor at the interface in terms of the barrier height, $(\phi_1-\chi_2)$, is

$(\phi_1-\chi_2)$ ev	1.0	0.5	0.1
N_0 (cm^{-3})	10^2	10^{10}	10^{17}

ϕ_1 and ϕ_2 are the work functions of the metal and semiconductor respectively; χ_2 is the electron affinity of the semiconductor.

The ac and dc measurements contain essentially the same information and illustrate the important properties of a thin insulating crystal of CdS with ohmic contacts, namely that the current in the dark is time-dependent and increases more rapidly than the square of the voltage across the crystal. With light on the crystal the photocurrent is proportional to the voltage until exceeded by the space-charge-limited current.

Crystal imperfections or traps in CdS account for the time dependence of the space-charge current and for the deviation from the theoretical square-law V–I characteristic for a perfect insulator to a power law or exponential variation.[3] More detailed experimental and analytical descriptions of the space-charge currents in CdS are given in papers by Smith and Rose[11] and by Rose.[12] Briefly the mechanism proposed is as follows: The ohmic contact to the insulator provides a reservoir of electrons with free access to the conduction band of the crystal. With the application of the electric field carriers are injected into the conduction band of the insulator and, for a perfect crystal, the current is given by the square-law (2). For an imperfect crystal most of the charge injected into the conduction band falls into traps where it cannot take part in conduction. Imperfections reduce the drift mobility, μ, in a way determined by the density and distribution of traps. The initial burst of current observed when the voltage is changed is the current passed before appreciable trapping takes place. The subsequent decay of the current to a stationary value is the effect of charge being trapped from the conduction band. The rate of decay depends on the density of electrons in the conduction band and the capture cross section of the traps.

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[12] A. Rose, accompanying paper [Phys. Rev. 97, 1538 (1955)].

Finally, it can be shown that the distribution of traps can determine the form of the V–I characteristic. In particular, if the distribution of traps is uniform in energy below the conduction band the current varies as $e^{\alpha V}$.

V. DISCUSSION

In the previous sections, it is shown that the usual materials used for electrodes to CdS do not readily make good reliable contact. It is shown that In and Ga do make good ohmic contact. The degree of perfection is indicated by the noise measurements of Shulman,[5] by the measurements of space-charge-limited currents, and by the low-voltage performance as a photoconductor.

It is believed that these results can be interpreted in terms of the basic theory[13,14] of the contact between a metal and a semiconductor. The generally accepted view of the contact is shown in Fig. 6, which is drawn specifically for an n-type semiconductor. When a metal of work function ϕ_1 is joined to a semiconductor of work function ϕ_2, a dipole layer is formed such as to produce a potential drop from the metal to the interior of the semiconductor equal to $(\phi_1-\phi_2)$. The height of the potential hill determines the degree of rectification of the contact and in particular determines the supply of carriers available to the semiconductor or insulator and the ease with which they can be injected. Metals for which $\phi_1 \gg \phi_2$ make rectifying contact, as for example Ag, or Au on CdS. For metals with low-work function, $\phi_1 \approx \phi_2$, the barrier height may be negligibly small and the supply of carriers available at the interface large. In short the contact is ohmic. Most of the low-work-function metals are extremely reactive chemically and so in practice are not suitable for electrodes. The work function of In and Ga is estimated[15–17] to be 3–4 ev and the metals seem to be chemically suitable. Furthermore it has generally been found that there is poor correlation between the degree of rectification and the work function of the metal making contact to a semiconductor. Bardeen accounts for the lack of correlation in terms of a shielding effect of surface states on the semiconductor. It is suggested that the case of In on CdS is one in which the low-work function of In overbalances the effect of surface states to the extent of actually reversing the curvature of the band structure at the surface from a rectifying to an ohmic pattern. It is suggested then that the noble metals make rectifying, nonohmic contact to CdS because their work functions are large compared with CdS and that In and Ga make ohmic contact because their work function is equal to or less than that of CdS.

The basic and important feature of an ohmic contact between a metal and a semiconductor is that the metal serves as a reservoir of carriers with free access to the conduction band of the semiconductor. This property of an ohmic contact, in addition to the fact that CdS can be made in relatively perfect single crystals, makes possible the observation of the space-charge-limited currents reported. The magnitude of the currents drawn indicate that the barrier height at the CdS-In interface must be less than or equal to 0.1 ev.

The author acknowledges the suggestions and discussions with Dr. A. Rose throughout this work.

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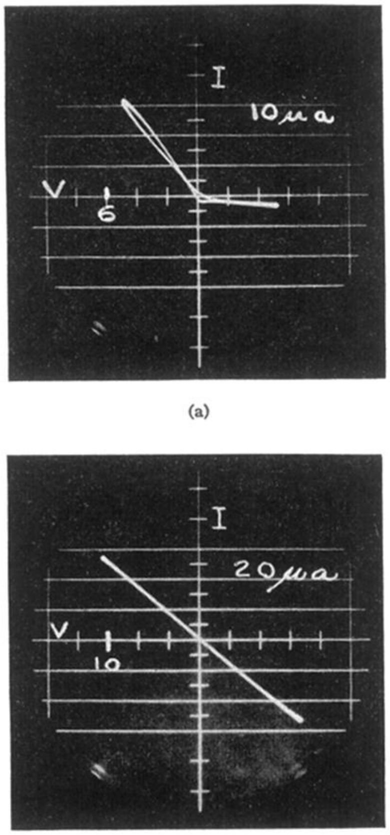
[13] See reference 2, also pp. 174–185.

[14] J. Bardeen, Phys. Rev. **71**, 717 (1947).

[15] H. B. Michaelson, J. Appl. Phys. **21**, 536 (1950).

[16] It is instructive to plot the known work functions of the elements against their ionization potential. From this correlation one estimates a work function ~3 ev for In and Ga.

[17] By means of television scanning, A. D. Cope of these Laboratories has measured the relative work functions of CdS, Ga, and Au. One face of a highly conducting CdS crystal was partly covered with separate Au and Ga dots. The landing potential of a low-velocity scanning beam was measured for each of the three regions. Assuming $\phi_{\mathrm{Au}}=4.9$ ev we get $\phi_{\mathrm{Ga}}=3.6$ and $\phi_{\mathrm{CdS}}=4.2$ ev.



(a)

(b)

Fig. 1. Oscilloscope traces of V–I characteristics of similar insulating, photosensitive CdS crystals. (a) Typical nonlinear trace obtained with the usual electrode materials, in this case Au. (b) Linear characteristics obtained with In electrode.

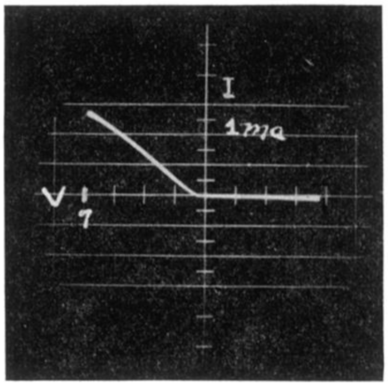


Fig. 3. Oscilloscope trace of V–I characteristic of broad area rectifier-photoconductive cell. Semitransparent Au electrode and opaque In electrode on insulating photosensitive CdS crystal. Room irradiation.