High Electric Fields in Cadmium Sulfide: Field-Effect Constriction of Current Flow and Dielectric Breakdown*

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Field-effect measurements have been employed to study constriction of current flow in very thin single crystals of conducting CdS. With an electrolyte field electrode and crystals having about 1 ohm-cm resistivity, it has been possible to obtain complete pinch-off of current flow through the crystal by applying voltage to the field electrode. The technique used is evaluated quantitatively and is found to be a satisfactory method for obtaining high electric fields of known magnitude in CdS. Dielectric breakdown occurs when sufficiently high voltage is applied to the field electrode. The breakdown field strength was found to be 1.8×10^6 v/cm at 25°C.

SEVERAL interesting properties of solids require, for their study, the production of a high electric field in a crystal of an insulator. A voltage must be applied to a suitably dimensioned specimen in such a way that the injection of carriers from the electrodes is at a minimum and the distribution of the field within the specimen is known. Use of an electrolyte solution as a blocking electrode on a crystal of conducting CdS permits high fields to be established within the crystal across a carrier-free space charge region adjacent to the electrode.[1,2] Injection of carriers from the electrode is minimal with this arrangement. To be confident of the distribution of the field within the crystal it is desirable to have a quantitative test showing how well the relevant theoretical model of the space charge region is able to describe experiments with this electrode arrangement. In the work described below, field-effect current pinch experiments are used to test the applicability of the Mott-Schottky model which relates the thickness of the space charge region at the field electrode to the applied voltage.[3] Results show that, under these conditions, the space charge region is adequately described by the Mott-Schottky model with a uniform volume distribution of donor centers.

When sufficiently high voltages are applied to the field electrode, dielectric breakdown occurs, followed by destruction of the crystal at the interface with the electrolyte. The model used to describe the space charge region is then used with experimental data to obtain the field strength at which dielectric breakdown occurs.

EXPERIMENTAL

The excellent blocking contact which an electrolyte solution makes to CdS allows its use as a field electrode to pinch off current flow in thin conducting crystals, without need of the dielectric spacer commonly employed in field effect measurements. Vapor-grown CdS crystals were used. These were grown in this laboratory by C. Busanovich and S. M. Thomsen. The conductivity was *n* type and due to either bromine or chlorine incorporated during growth. There was no observable difference between chlorine and bromine doped crystals for the type of experiments done here. The halogens, when incorporated in CdS, form shallow donor levels lying several hundredths of an electron volt below the conduction band.[4] These levels are completely ionized at room temperature and result, for the crystals used here, in dark resistivities ranging from about 0.2 to 10 ohm-cm.

The crystals grew in the form of thin ribbons about 1 cm long, 0.05 cm wide, and with thicknesses ranging from 2 μ up to 15 μ. Most crystals were used as grown. Some were etched in 7.0 *M* HCl to reduce their thickness. The properties of crystals which had been etched were no different, in the field effect measurements, from the properties of crystals with similar final thickness which had not been etched. Crystal thicknesses were measured by mounting in a vertical plane and viewing the thin edge of the crystal in vertical illumination through a microscope fitted with a calibrated scale in the eyepiece. The precision of this method is about $\pm5\%$ for thicknesses above 5 μ and about $\pm10\%$ for the smaller thicknesses.

CdS ordinarily crystallizes in the hexagonal wurtzite lattice. In the crystals used here, the *c* axis was in the plane of the thin ribbon and perpendicular to the long dimension of the ribbon. This is of importance in connection with the dielectric breakdown experiments which show pronounced anisotropy.

The mounting of crystals and electrical connections are best explained with reference to Fig. 1. Ohmic contacts were applied to the ends of a ribbon crystal by brushing on a fused alloy containing equal parts of gallium and indium. The crystal was mounted on a ring of Glyptal resin which served to hold it and to contain an electrolyte solution so that the electrolyte could surround the center section of the crystal without coming into contact with the ohmic electrodes at the ends of the crystal. In operation, the ring was filled nearly to the top with 0.1 *M* water solution of KCl, which

* This work was supported in part by a Naval Ordnance government contract.
[1] R. Williams, Phys. Rev. **117**, 1487 (1960).
[2] R. Williams, J. Chem. Phys. **32**, 1505 (1960).
[3] H. K. Henisch, *Rectifying Semiconductor Contacts* (Oxford University Press, New York, 1957), p. 189.
[4] R. H. Bube and S. M. Thomsen, J. Chem. Phys. **23**, 15 (1955).

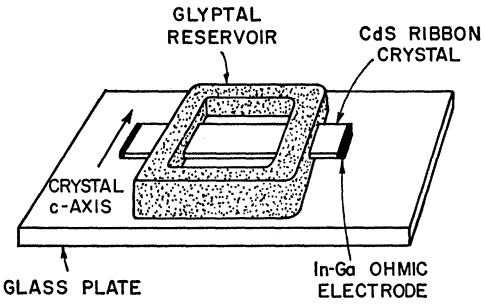

FIG. 1. Method of mounting thin CdS crystals for field-effect measurements. The field electrode is an electrolyte solution which fills the reservoir and surrounds the center section of the crystal.

served as a field electrode encircling the crystal. Contact between the solution and the external circuit was made through a platinum wire. It was determined that there was no appreciable polarization occurring at the platinum wire for any of the current densities which were encountered. Thus, to a good approximation, the potential difference across the interface between the platinum wire and the solution was independent of applied voltage.

Figure 2 shows the circuit employed to study constriction of current flow through the crystal by dc voltage on the electrolyte field electrode. To make contact to the Ohmic end electrodes of the crystal, silver paste stripes were painted from the electrodes to metal tabs cemented on the glass base plate. V_1 and V_2 could be varied smoothly by means of Helipot potentiometers. The electrolyte solution makes blocking contact to the crystal only when the crystal is maintained at a potential positive with respect to the solution. Reversing the polarity of V_2 leads to high current flow and destruction of the surface of the crystal.[2] For this reason, the polarity shown in Fig. 2 was always maintained. Light was excluded from the crystal during field effect measurements to avoid light generated carriers in all experiments except those where the behavior of such carriers was being investigated explicitly.

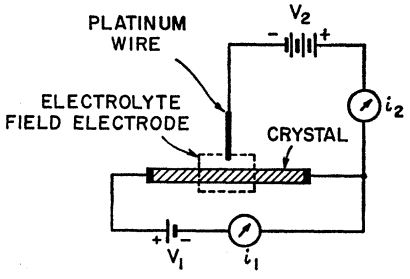

FIG. 2. Circuit connections for field-effect measurements. V_1 and V_2 are taken off Helipot potentiometers. The voltage drop in the meters for i_1 and i_2 is negligible compared to the respective values of V_1 and V_2.

RESULTS AND EXPERIMENTS

With increasing values of V_2, the voltage applied to the field electrode, the thickness, λ, of the space charge region in the crystal increases. The electrolyte field electrode is always negative with respect to the crystal. Under these conditions the space charge region in the crystal results from positive ionized donor centers whose electrons have been removed from the crystal in order to establish the voltage on the field electrode. The equivalent negative charge has been placed on the surface of the crystal in the form of negative ions from solution. The space charge region is devoid of free charge carriers and as it becomes thicker it fills more of the crystal and reduces the effective cross section for current flow. This behavior has been analyzed in detail by Shockley[5] and is described here to make clear the function of the several components of the present arrangement.

Measurements were made of the current i_1, through the crystal for various values of V_2, keeping V_1 constant. (Definition of terms is in Fig. 2. $V_1 \ll V_2$ and $i_2 \ll i_1$.) Figure 3 shows results of such a measurement for two different values of V_1. The current through the crystal is pinched off approximately linearly as V_2 is increased. It is completely pinched off when $V_2 \approx 35$ v and remains so as V_2 is increased further. When V_2 is removed, the current returns to its original value and after many measurements over several days time there is no change in the appearance or properties of the crystal. The frequency response of the effect has not yet been determined and, at present, it can only be said that the response occurs in less than a tenth of a second. The current i_2 is small compared to i_1 but increases with increasing V_2. Its magnitude at the pinch-off voltage, V_p, is generally about 10^{-4} times the amount of current which has been pinched off.

To compare the data with theory we employ the Mott-Schottky equation in the form given by Henisch.[3] The thickness, λ, of the space charge region is given by

$$\lambda^2 = \frac{\epsilon}{2\pi N e}(V_D + V_B), \tag{1}$$

where ϵ = the static dielectric constant of the crystal, N = number of ionized donor centers/cc, e = electronic charge, V_D = diffusion voltage, and V_B = externally applied voltage. The concept of diffusion voltage is not simple for a system including an electrolyte, which is not an electronic conductor. A detailed discussion has been given by Dewald.[6] The appropriate quantity has the order of magnitude of 1 v. Since the applied voltages in the current pinch experiments are much larger than 1 v over most of their range, the quantity $V_D + V_B$

[5] W. Shockley, Proc. Inst. Radio Engrs. **40**, 1365 (1952).
[6] J. F. Dewald, *Semiconductors*, edited by N. F. Hannay (Reinhold Company, New York, 1959), Chap. 17.

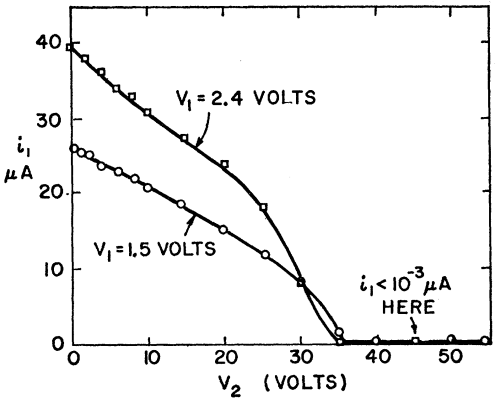

FIG. 3. Pinching-off of current flow, i_1, by the field electrode voltage, V_2. The two curves are for two different values of V_1. V_1 is constant for all points on a given curve and is much smaller than V_2 over most of the curve.

will be replaced by the experimental quantity, V_2. Using the value of 11.6 for the static dielectric constant of CdS,[7] Eq. (1) takes the form:

$$\lambda = 3.6\times 10^3 (V_2/N)^{\frac{1}{2}} \text{ cm}. \tag{2}$$

The derivation of Eq. (1) assumes a uniform volume distribution of donors. In this work the value of N is obtained from measured values of resistivity, using the reported value[8] of the bulk electron mobility in CdS of 210 cm²/v-sec.

To compare Eq. (2) with the data, it may be recalled that the complete pinch-off of current by the field electrode occurs when the space charge region is thick enough to fill the entire crystal. Since the space charge regions from the two opposite broad faces penetrate into the crystal and meet at the center, the pinch-off occurs when each of them is half the total thickness of the crystal. This gives the experimental thickness of the space charge region at the pinch-off voltage, V_p, from the measured crystal thickness. The thickness is then calculated from Eq. (2) for $V_2 = V_p$, using the measured value of N. Values of experimental and calculated thicknesses for several different crystals are given in Table I. The agreement is satisfactory, considering that an absolute calculation of λ is involved. The small systematic difference between experimental and theoretical values could easily be due to error in the values of mobility and dielectric constant used in the calculation.

A further test of Eq. (2) is to examine the variation of λ with V_2 bearing in mind that the effective thickness of the crystal for current flow is the geometric thickness minus 2λ. In the case where the crystal is wide compared to its thickness and the field electrode extends the entire length of the crystal, Eq. (2) gives a very simple result for the experiments were V_1 is constant and small

[7] F. A. Kröger, H. J. Vink, and J. Volger, Philips Research Repts. **10**, 48 (1955).
[8] F. A. Kröger, H. J. Vink, and J. Volger, Philips Research Repts. **10**, 39 (1955).

TABLE I. Experimental test of Eq. (2), using field-effect current pinch data from nine different crystals. All measurements made at 25°C.

Voltage for complete pinch-off of current (volts)	ρ Measured crystal resistivity (ohm-cm)	λ_{calc} Calculated from Eq. (2) (microns)	λ_{exp} Half of measured crystal thickness (microns)	Fractional difference $(\lambda_{exp}-\lambda_{calc})/\lambda_{exp}$
11.6	2.05	1.0	1.1	+0.09
42	0.86	1.2	1.2	0
90	1.20	2.1	2.0	−0.05
35	1.92	1.7	2.0	+0.15
45	1.13	1.5	2.0	+0.25
80	1.08	1.9	2.4	+0.21
44	2.46	2.1	2.4	+0.12
140	1.23	2.6	2.4	−0.08
105	2.57	3.4	4.3	+0.21
	Average value of $(\lambda_{exp}-\lambda_{calc})/\lambda_{exp} = +0.09$			

compared to V_2. This is

$$i_1(V_2)/i_1(0) = 1-(V_2/V_p)^{\frac{1}{2}}, \tag{3}$$

where $i_1(0)$ is the value of i_1 when $V_2 = 0$. Derivations of this and a more general case were given by Shockley.[5] A modification of Eq. (3) must be made to treat the present data. As may be seen from Fig. 1, the field electrode in these experiments does not cover the entire length of the crystal. Because of the small dimensions involved and the need to prevent the electrolyte from reaching the end contacts, the field electrode was significantly shorter than the total length of the crystal. With a voltage applied to the ends of the crystal and with $V_2 = 0$, there is a uniform field throughout the crystal in the direction of current flow. When V_2 is increased, the resistance increases in the center section of the crystal covered by the field electrode. With constant V_1, the field in the direction of current flow in the center section becomes larger as a result of this increased resistance. For this reason, the current flow is not pinched off as much as Eq. (3) predicts. The appropriate correction is easily made. A parameter, ϕ, is defined as the ratio of the total resistance of the end sections of the crystal, not covered by the field electrode, to the resistance of the center section which is covered by the field electrode; both for $V_2 = 0$. The parameter may be measured by measuring the appropriate lengths since the crystals have uniform cross section. The modified form of Eq. (3) now becomes

$$\frac{i_1(V_2)}{i_1(0)} = \left[1-\left(\frac{V_2}{V_p}\right)^{\frac{1}{2}}\right]\frac{1+\phi}{1+\phi[1-(V_2/V_p)^{\frac{1}{2}}]}. \tag{4}$$

Figure 4 shows current pinch data for two representative crystals of different thickness. For comparison, a plot of Eq. (4) for the appropriate value of ϕ is included for each crystal. The agreement indicates the validity of Eq. (4) and demonstrates an approximately uniform volume distribution of donors.

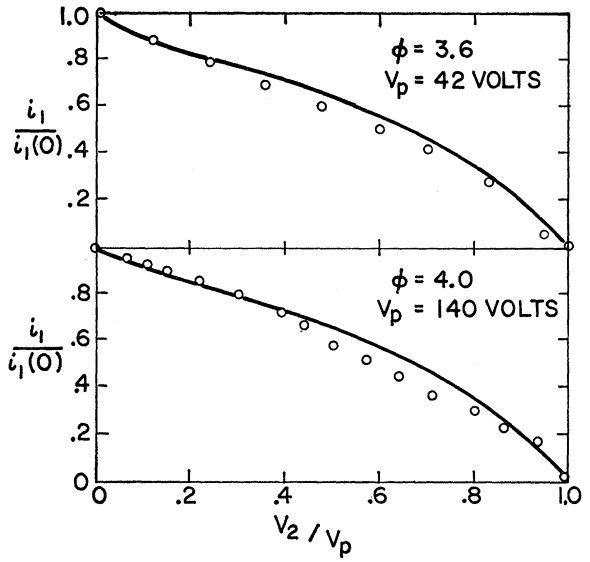

FIG. 4. Current pinch-off for various values of field-electrode voltage compared with Eq. (4). Circles are experimental data and solid lines are calculated from Eq. (4) for the appropriate value of ϕ.

From the data of Fig. 4 and Table I it is concluded that the magnitude and spatial variation of the potential in the crystal are described, to a good approximation, by the Mott-Schottky model for a space charge region with a uniform volume distribution of donors.

DIELECTRIC BREAKDOWN

When a crystal specimen is used which is somewhat thicker than those described above, dielectric breakdown occurs before a voltage high enough to cause complete current pinch-off is reached. This is indicated by a very steep rise of the current in the field electrode circuit with increasing values of V_2. Sudden pulses of current flow as successive areas of the crystal surface break down. There is no evidence that heating raises the temperature substantially in the prebreakdown region and it appears to be a true electronic breakdown which leads to the destruction of the surface. Extensive studies by Böer and co-workers[9] on dielectric breakdown in CdS have delineated the conditions which lead to true electronic breakdown as opposed to thermal breakdown. The conditions of the present experiments are similar to those which these workers found to give electronic breakdown.

The chief qualitative feature of interest is that the breakdown nearly always occurs along one edge of the crystal. As can be seen from Fig. 1, the electrolyte surrounds the center section of the crystal. The electric field within the crystal is everywhere perpendicular to the surface. The two narrow faces perpendicular to the c axis are not equivalent since the hexagonal wurtzite structure lacks a center of symmetry. The breakdown appears to start on one of these narrow faces and spread to the broad side faces, with the extent of this spreading differing from crystal to crystal. Figure 5 shows an example of a breakdown which has spread far enough onto the side faces to be readily visible. There is no visible roughness or surface structure on the breakdown face which might lead to breakdown merely by concentration of the electric field geometrically. In some cases the breakdown destruction is in the form of small separated spots on one edge rather than a continuous area as in Fig. 5. The (0001) face of a CdS crystal may be distinguished experimentally from the (000$\bar{1}$) face by examination of etch figures produced in acid solutions.[10,11] Hexagonal etch pits are formed on (0001),

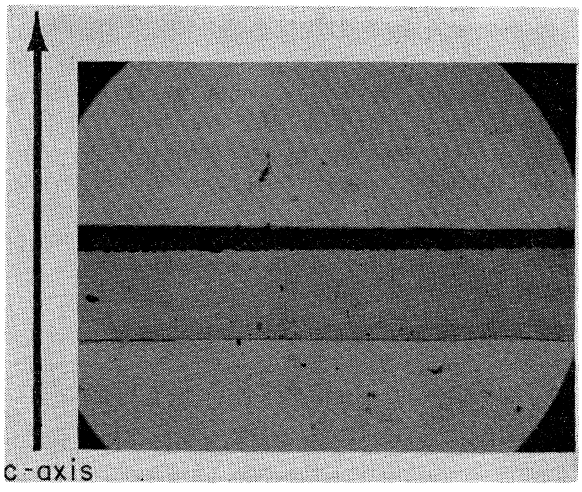

FIG. 5. Photograph of destructive dielectric breakdown along the edge of a CdS crystal. The electrolyte electrode surrounded this section of the crystal and the applied field was directed perpendicular to the surface at all points. The plane of the thin crystal lies in the plane of the page. Width of crystal is 0.5 mm.

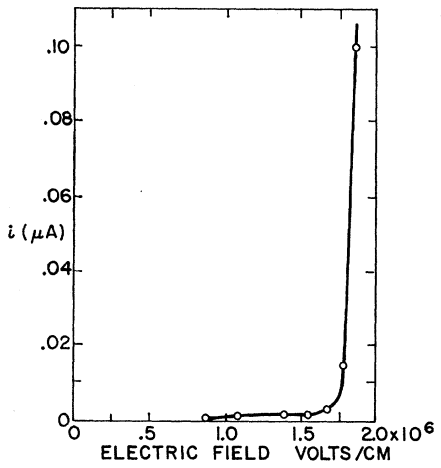

FIG. 6. Prebreakdown current versus the maximum field strength within the crystal.

[9] K. W. Böer and U. Kümmel, Ann. Physik **14**, 341 (1954); **16**, 181 (1955).
[10] J. Woods, Brit. J. Appl. Phys. **11**, 296 (1960).
[11] D. C. Reynolds and S. J. Czyzak, J. Appl. Phys. **31**, 94 (1960).

while on $(000\bar{1})$ there are formed either conical pits or uniform roughening of the surface, depending on the etch employed. This technique was applied to five crystals on which the edge breakdown described above had been produced. The etching was done on portions of the crystals near the ends which had not been exposed to the electrolyte and had suffered no surface damage. In all cases the breakdown had occurred at the face on which hexagonal etch pits were produced; i.e., (0001) in the notation of reference 10. Thus, there is either a preferred crystal face less resistant to breakdown than the others or, alternatively, there is a direction within the crystal having a particular polarity with respect to the c axis, along which the field most readily causes breakdown.

BREAKDOWN FIELD STRENGTH

For these measurements, V_1 and the current meter for i_1 was removed from the circuit of Fig. 2. As V_2 is steadily increased, there is a region where i_2 is small and then a steep rise in i_2, followed by destructive breakdown. A typical result is shown in Fig. 6. Because of the steep rise of current with voltage just before breakdown, it is possible to define the breakdown voltage arbitrarily as the voltage at which the current reaches a certain value, chosen here as 1 μamp. As in preceding sections, the value of λ is obtained from the Mott-Schottky equation for the value of V_2 at which breakdown occurs. The average field within the space charge region for any applied voltage is V_2/λ. At the inner edge of the space charge region the field is zero and it increases linearly with distance until it reaches a maximum value at the interface with the electrolyte. Hence the maximum value of the field is twice the average value. It is, of course, the maximum value which should be taken as the breakdown field strength. Table II contains values of the breakdown field strength obtained in this way for several crystals.

BEHAVIOR OF INJECTED CARRIERS

In considering the mechanism of the breakdown, it is of interest to know the behavior of carriers in the space charge region as the field is increased. As in the experiments described in the preceding paragraph, V_2 was increased steadily and the resulting current measured. To inject carriers, the crystal was illuminated during the measurement with light of 450 mμ wavelength from a monochromator. The absorption coefficient for light of this wavelength[12] in CdS is about 10^5 cm^{-1}, so most of the light is absorbed within a tenth of a micron from the surface. Under the action of the field, the electron produced by the light moves toward the interior of the crystal and the hole moves toward the surface. The potential within the space charge region is a parabolic function of distance along the field direction. In a representative case of interest where a voltage is applied sufficient to make the thickness of the space charge 1 μ, a typical electron produced by the light traverses 90% of the length of the space charge region and falls through a potential equal to 80% of the applied voltage, providing no trapping occurs. The conditions are thus provided where multiplication of carriers by impact ionization might be detected. Figure 7 shows an i–V curve obtained with this arrangement. It is seen that there is a long range of voltage where there is a saturated photocurrent of approximately one electron per incident photon. In this region it is clear that impact ionization is *not* occurring. The steep noisy rise of current near 80 v might be due either to impact ionization or to a steeply rising tunneling current of carriers from the valence band, deep traps, or the electrode. Since this steep rise coincides with that of the prebreakdown current in the unilluminated crystal, it is not possible to say from this experiment alone whether this rise in current is due to impact ionization which also initiates the breakdown or whether there is no impact ionization and the steep rise is due to a tunnel current superimposed on the constant current of the

TABLE II. Measured values of dielectric breakdown field strength in CdS. All measurements made at 25°C.

Crystal specimen No.	Applied voltage at breakdown (volts)	Breakdown field strength, F (volts/cm)
1	90	1.6×10^6
2	75	2.3×10^6
3	90	2.2×10^6
4	100	2.1×10^6
5	130	0.85×10^6
	Average value of $F=(1.8\pm0.3)\times10^6$	

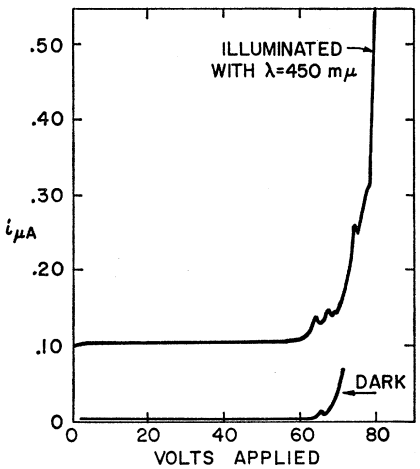

FIG. 7. Comparison of pre-breakdown currents in the same crystal in the dark and when illuminated with strongly absorbed light. With light-injected carriers there is a long voltage range in which there is a saturated current of approximately one electron per incident photon. This is followed by a very steeply rising and noisy current. Curves copied from a recorder tracing.

[12] J. F. Hall, J. Opt. Soc. Am. **46**, 1013 (1956) and ref. 20.

light-injected carriers. If one assumes that the field in the space charge region is not greatly altered by the presence of light-injected carriers, then it is possible to specify a minimum field below which impact ionization does not occur. This value is 1.6×10^6 v/cm for the crystal used for Fig. 7. There is some support for the contention that impact ionization does not occur and that the rise in current is due to a tunneling process. This will be brought out in the discussion.

DISCUSSION

The anisotropy of the breakdown produced by a symmetrical electrode arrangement illustrates the importance of crystal symmetry in the breakdown process. Davisson has shown that, for a variety of crystals, the breakdown paths conform to the point group symmetry of the crystal.[13,14] For noncentrosymmetric crystals the breakdown paths should conform to this lack of symmetry and slightly different breakdown strengths at different faces would arise for the electrode arrangement used here.[15] A more detailed discussion of this requires further knowledge of the mechanism of breakdown.

The theories of dielectric breakdown most relevant to the present experiments are the impact ionization theory of Fröhlich[16] and the tunneling theories discussed extensively by Franz[17] and Böer.[18] An approximate quantitative comparison of the present work can be made with the treatments of Fröhlich and Franz and the discussion will be confined to these.

Fröhlich gives an equation for the breakdown field strength, F, which is in excellent agreement with experiment for the alkali halides, and which assumes impact ionization as the process initiating breakdown. The equation is

$$F=1.64\times10^5\left(\frac{d}{G}\right)^{\frac{1}{4}}(\epsilon-\epsilon_0)\frac{\lambda_0}{\lambda_1^{\frac{3}{2}}}\left(1+\frac{1}{e^{h\nu/kT}-1}\right)^{\frac{1}{2}}, \quad (5)$$

with F in v/cm. Here d=density in g/cc, G=molecular weight, ϵ=static dielectric constant, ϵ_0=high-frequency dielectric constant (square of the refractive index for near infrared wavelengths), λ_0=wavelength in A of optical band edge, and λ_1=wavelength in microns of reststrahlen absorption whose frequency is ν. (Recent measurements indicate $\lambda_1=38.5\,\mu$.)

It is of interest to estimate the breakdown field which the equation predicts for CdS. Using the value 5.3 for ϵ_0,[19] 11.6 for ϵ, 5100 A for λ_0,[20] 38.5 μ for λ_1,[21] and 33 for G/d, we arrive at the result:

$$F=7.7\times10^6 \text{ v/cm}.$$

This is about an order of magnitude higher than the value which the same equation predicts for the alkali halides. It is in agreement with the evidence presented in the previous section that impact ionization does *not* occur at any field strengths less than 1.6×10^6 v/cm. However, the difference between the predicted value and the observed breakdown field strength of 1.8×10^6 appears to be outside the limits of error in the measurements. Questions have been raised concerning the validity of Eq. (5) and these are reviewed in reference 17. Tentatively, we accept the discrepancy between calculated and observed breakdown field strengths as an indication that the breakdown is not initiated by impact ionization in order to consider an alternative hypothesis.

The process of electron tunneling from valence band to conduction band of an insulator in an electric field has been extensively treated. The tunneling leads to a current which rises very rapidly with increasing field and could initiate destructive dielectric breakdown. A theoretical expression for the probability of this kind of tunneling has been given by Franz[22] who discusses the problem with explicit reference to dielectric breakdown. The transition probability, w, that an electron shall tunnel from valence band to conduction band is given by

$$\log_{10}w(\text{sec}^{-1})=\log_{10}(4.6\times10^{-13}AF^{10/3})-1.75\times10^7(m^*/m)^{\frac{1}{2}}J^{\frac{3}{2}}/F, \quad (6)$$

where m^*/m=electron effective mass ratio, J=optical band gap (2.44 ev for CdS), F=electric field in volts/cm, and A=a complicated function whose order of magnitude is unity. It is the last term which dominates the dependence of transition probability on field. Tunneling becomes important[22] when the quantity in the last term is about 15. The field for which this is true may be readily calculated, then, if the electron effective mass is known. Reported values of m^*/m for CdS range from 0.15 to 0.35.[23] For these two values, the critical field strengths are 1.6×10^6 and 2.3×10^6 v/cm, respectively. The observed breakdown field strength lies between these two numbers. This approximate numerical agreement with theory may mean that the breakdown process observed here is a true intrinsic breakdown initiated by tunneling of electrons from valence band to conduction band. There is other evidence in

[13] J. W. Davisson, Acta. Cryst. **9**, 9 (1956).
[14] J. W. Davisson, in *Progress in Dielectrics* (John Wiley & Sons, Inc., New York, 1959), Vol. 1, pp. 59–96.
[15] J. W. Davisson (private communication).
[16] H. Fröhlich, Proc. Roy. Soc. **A188**, 230 (1937). H. Fröhlich and J. H. Simpson, in *Advances in Electronics*, edited by L. Marton (Academic Press, Inc., New York, 1950), Vol. II, pp. 185–216.
[17] W. Franz, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 17, pp. 155–263.
[18] K. W. Böer and U. Kümmel, Ann. Physik **14**, 341 (1954).
[19] S. J. Czyzak, W. M. Baker, R. C. Crane, and J. B. Howe, J. Opt. Soc. Am. **47**, 240 (1957).
[20] D. Dutton, Phys. Rev. **112**, 785 (1958).
[21] A. Mitsuishi, H. Yoshinaga, and S. Fujita, J. Phys. Soc. Japan **13**, 1235 (1958).
[22] Reference 17, p. 215.
[23] R. N. Dexter, J. Phys. Chem. Solids **8**, 494 (1959), also reference 8.

support of this idea. If tunneling from valence band to conduction band occurs at a certain value of the field according to the theory, then identical theoretical considerations show that, for somewhat lower fields, there should be an observable shift of the optical band edge on applying the field.[24] This effect has been observed in CdS using the same electrode arrangement employed here.[1] Results are in good qualitative and quantitative agreement with theory and the effect does, indeed occur for field strengths just lower than that which produces breakdown. The shift of the band edge with field is attributed to a precursor of tunneling in which electrons from the valence band penetrate part way into the forbidden energy gap but do not cross completely through to the conduction band.

Though the evidence presented here is in agreement with the hypothesis that breakdown is initiated by tunneling, many features of the data could be explained equally well as impact ionization. In addition, the use of existing theories for the absolute calculation of breakdown field strength is probably a treacherous procedure, though a worthwhile one in bringing out the relation of theory to experiment. Further experiments are in progress to study more extensively the current-voltage characteristic in the pre-breakdown region and establish more firmly the mechanism of breakdown.

An earlier measurement of the breakdown field strength by Böer and Kümmel[18] gave values around 10^5 v/cm. The properties of their crystals, as well as the electrode arrangement, were quite different from those used here so a direct comparison of results is difficult. It appears likely that breakdown was initiated by a different process before the field strength was reached necessary for the process observed here. They also observed prebreakdown currents showing a general resemblance to those of Figs. 6 and 7.

[24] W. Franz, Z. Naturforsch. **13a**, 484 (1958).

SUMMARY

A technique has been evaluated for the production and study of high electric fields of known magnitude in single crystals of CdS. Fields were produced by applying voltage to an electrolyte blocking electrode in contact with a conducting crystal. The field occurs in a space charge region approximately a micron thick within the crystal. A quantitative description of the properties of the space charge region is found to be given by the Mott-Schottky equation. This was demonstrated by field-effect current pinch experiments with very thin crystals. Dielectric breakdown occurs for fields of 1.8×10^6 v/cm. With a symmetrical electrode arrangement, the breakdown is unsymmetrical, in agreement with the point group symmetry of the CdS crystal. Comparison of the measured breakdown field strength with existing theories of dielectric breakdown is made. Results agree with the interpretation that the breakdown is initiated by tunneling of electrons from valence band to conduction band though the hypothesis that impact ionization also takes place cannot be excluded.

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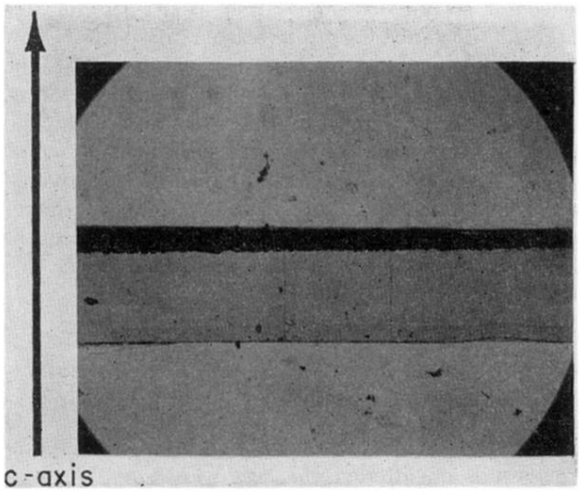

FIG. 5. Photograph of destructive dielectric breakdown along the edge of a CdS crystal. The electrolyte electrode surrounded this section of the crystal and the applied field was directed perpendicular to the surface at all points. The plane of the thin crystal lies in the plane of the page. Width of crystal is 0.5 mm.