

## Densitometric and Electrical Investigation of Boron in Silicon

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New analytical, x-ray diffraction, precision density, and electrical resistivity studies of boron-doped silicon show that boron resides in the silicon lattice substitutionally.

### INTRODUCTION

PEARSON and Bardeen<sup>1</sup> and more recently Morin and Maita<sup>2</sup> have investigated the electrical properties of silicon containing boron. Pearson and Bardeen concluded from electrical and lattice parameter studies that boron occupies substitutional positions in the silicon lattice. In the present investigation density measurements in addition to lattice parameters, electrical, and chemical analysis, confirm the location of boron as substitutional in silicon up to concentrations of 0.3 atom percent.

### PREPARATION OF SAMPLES

There is no ready source of boron of a purity comparable to that of silicon currently available. Most elements have a smaller segregation coefficient ( $C_s/C_l$ ) than boron in silicon.<sup>3,4</sup> It is possible to make use of this difference to remove impurities introduced with the boron in silicon itself. Thus, if boron with impurities that segregate during crystallization of silicon is added to silicon which is then zone-melted,<sup>5</sup> the first frozen region of the zone-refined ingot will still contain boron but, in accordance with their segregation constants, the impurities will be swept out to crystallize toward the sprout end.

For these studies, approximately one atom percent of Norton "spec. fine" boron was added to zone-refined DuPont hyperpure silicon. This solution was zone-refined, five zones being used. Weighed portions of about the second 40 percent of the zone-refined ingot were added to known weights of zone-refined silicon and single crystals grown. Slices of single crystal were taken from as nearly the same region of each crystal as possible in order to minimize the effects of segregation of boron down the length of a crystal. Where chemical analyses for boron were made, the pieces were taken adjacent to the slices retained for study. The samples prepared and their boron content are listed in Columns I and II of Table I.<sup>6</sup>

<sup>1</sup> G. L. Pearson and J. Bardeen, *Phys. Rev.* **75**, 865 (1949).

<sup>2</sup> F. J. Morin and J. P. Maita, *Phys. Rev.* **96**, 28 (1954).

<sup>3</sup> R. N. Hall, *J. Phys. Chem.* **57**, 836 (1953). Note: Gallium should be 0.004.

<sup>4</sup> E. A. Taft and F. H. Horn, *Phys. Rev.* **93**, 64 (1954).

<sup>5</sup> W. G. Pfann, *J. Metals* **80**, 747 (1952).

<sup>6</sup> I am indebted to W. W. Welbon of the Analytical Section, Chemistry Department for these boron analyses. The method used was worked out by Dr. E. H. Winslow of this laboratory.

### PRECISION DENSITY MEASUREMENTS

In order to establish the location of boron in a silicon crystal the x-ray diffraction data require confirmation by density measurements. Since only very small concentrations of boron are necessary to alter the electrical properties of silicon greatly, it was considered desirable to use a method that would measure extremely small density changes with high precision. An adaptation of a "density gradient" method developed by Linderstrom-Lang<sup>7</sup> was tested and used in these studies. Details for the preparation, use, and accuracy of the method are discussed in the Appendix. The methods used in this study were accurate to  $10^{-5}$  g/cc while the sensitivity was about  $3 \times 10^{-7}$  g/cc.

### DENSITY OF SILICON

As a check on the operation of the density columns, the density of a 40 ohm-cm piece of silicon (DuPont, zone refined and grown single crystal) was determined. The results, taken from measurements that varied  $2 \times 10^{-6}$  over 48 hours are given in Table II.

Other previous calculations or measurements have been included. Since the time of these measurements we have found a variation in the density of high-resistivity single-crystal silicon of the order of  $20 \times 10^{-6}$  g/cc. We have thus rounded the value reported to 2.33067 (25.3°C). This value compares favorably with the density 2.330<sup>5</sup> calculated from the x-ray diffraction  $a_0$  value determined on the same material.

TABLE I. Increase in density and lattice contraction from boron in silicon.

Crystal	Boron atom percent added	g/cc $\times 10^6$ greater than Si	$a_0$ in Å
RR-55	0.314 $\pm$ 16 <sup>a</sup>	1540 <sup>b</sup>	5.4249 $\pm$ 0.0010
RR-54	0.104 $\pm$ 17.5 <sup>a</sup>	315	5.4281 $\pm$ 0.0008
RR-53	0.052	189	5.4282 $\pm$ 0.0004
RR-52	0.021	88	5.4291 $\pm$ 0.0004
RR-51	0.0021	7	
RR-50	0.00021	5	
RR-49	0.000021	2	
Control		0	5.4295 $\pm$ 0.0005

<sup>a</sup> By chemical analysis; others by aliquot taken.

<sup>b</sup> Measured pycnometrically.

<sup>7</sup> K. Linderstrom-Lang and H. Lang, Jr., *Compt. rend. trav. lab. Carlsberg* **21**, 315 (1938); Linderstrom-Lang, Jacobsen, Johannsen, *Compt. rend. trav. lab. Carlsberg* **23**, 17-24 (1941).

TABLE II. Lattice parameter and density of silicon.

Worker	Year	Purity	$a_0$ in Å	$d$ g/cc
Lipson and Rogers <sup>a</sup>	1944	99.85%	5.4308	2.328 <sup>2b</sup>
Straumanis and Aka <sup>c</sup>	1952	0.01 ohm-cm +0.03%	5.431	2.328 <sup>3</sup> (20°C)
McSkimmin <i>et al.</i> <sup>d</sup>	1951			2.331
Decker <sup>e</sup>	1953	ca 40 ohm-cm	5.4295 ± 0.0005	2.330 <sup>5</sup> (25°C)
This study	1954	ca 40 ohm-cm		2.3306 <sup>7</sup>

<sup>a</sup> H. Lipson and L. E. R. Rogers, *Phil. Mag.* **35**, 544 (1944).

<sup>b</sup> Calculated by using  $N_A(\text{chem}) = 6.02402 \times 10^{23}$ ,  $\lambda_0/\lambda_s = 1.00203$ , from J. A. Bearden and H. M. Watts, *Phys. Rev.* **81**, 73, 160 (1951); and  $M_{Si} = 28.09$ —*Chem. Eng. News*, **29**, 4077 (1951).

<sup>c</sup> M. E. Straumanis and E. Z. Aka, *J. Appl. Phys.* **23**, 330 (1952).

<sup>d</sup> McSkimmin, Bond, Buehler, and Teal, *Phys. Rev.* **83**, 1080 (1951).

<sup>e</sup> I am indebted to Mrs. B. Decker of this laboratory for these data, the average of seven measurements.

### DENSITY OF BORON-DOPED SILICON

Spheres of boron-doped silicon were placed in a prepared density-gradient column together with the glass calibration spheres. After allowing a day for equilibration, the position of the spheres was read and by interpolation from the position of the calibration spheres translated into differences in density referred to 40 ohm-cm resistivity silicon. These values are reported in Table I, Column III.

It will be noted that the density increases with increasing boron concentration in the silicon. This was contrary to an expectation based on the assumption that the density change is the additive effect of the increase in the density caused by lattice contraction and the decrease in density caused by substituting the lighter boron atoms for the silicon. From Pearson and Bardeen's<sup>1</sup> data, the lattice contraction amounts to 0.115 percent per atom percent boron, or an increase of 0.345 percent in density. The density decrease due to a substitution of one atom percent boron for silicon is readily calculated to be 0.64 percent. From these considerations we had anticipated a *decrease* in density of the order 0.3 percent from boron doping. The observed *increase* in density amounted to about 0.2 percent. This increase could be explained if the boron atoms do not enter the silicon crystal entirely by substitution—*viz.*, as a precipitate or interstitially.

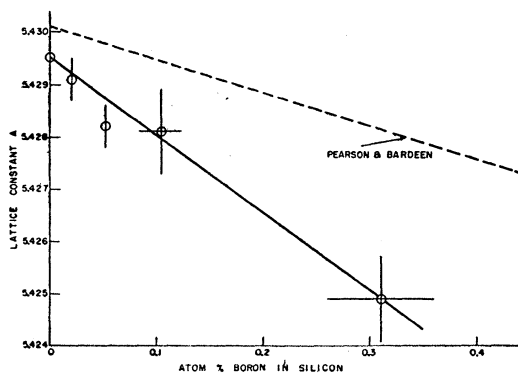


FIG. 1. Lattice constant for silicon as a function of boron concentration.

It seemed more reasonable, particularly because the electrical data of Pearson and Bardeen was in such good agreement with their assumption of substitutional boron, that the explanation might rather be found in some uncertainty of the lattice contraction data given by these authors. This seemed the more likely since Pearson and Bardeen were obliged to use polycrystalline silicon. Their composition scale could thus be in error due to boron rejection at grain boundaries. Such considerations led us to a redetermination of the lattice contraction due to boron.

The lattice parameters for the boron-doped silicon samples<sup>8</sup> are reported in Table I, Column IV. These values are compared with the results of Pearson and Bardeen in Fig. 1. It is observed that the lattice contraction determined in this study is considerably

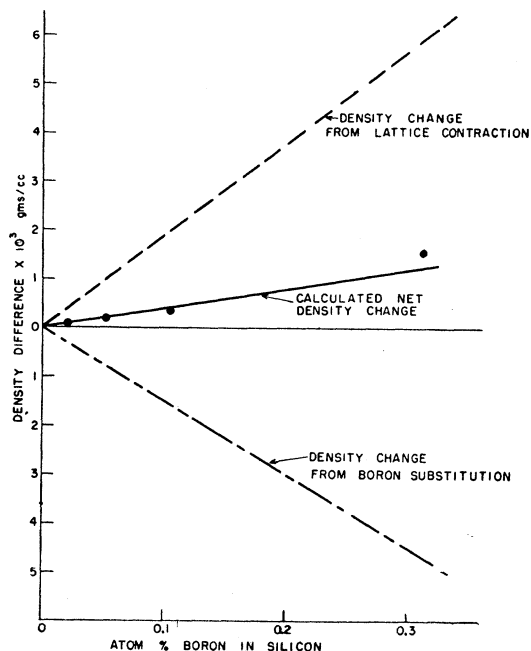


FIG. 2. Measured increase in density of silicon as a function of boron concentration compared with sum of density changes due to lattice contraction and boron substitution.

greater than that formerly reported. The contraction amounts to 0.86 percent in density in silicon as compared with 0.35 percent reported by Pearson and Bardeen.

The effect on the calculated density from our lattice contraction data is shown in Fig. 2. The lower curve is for the decrease in density calculated for the effect of boron substitution only. The sum of this curve and the density increase due to lattice contraction has also been indicated. It is seen that within the accuracy of the determination of the boron composition the measured densities agree well with the calculated net density change based on the assumption that this change is

<sup>8</sup> I am indebted to Mrs. A. Cooper of the Metallurgy Department for these x-ray diffraction determinations.

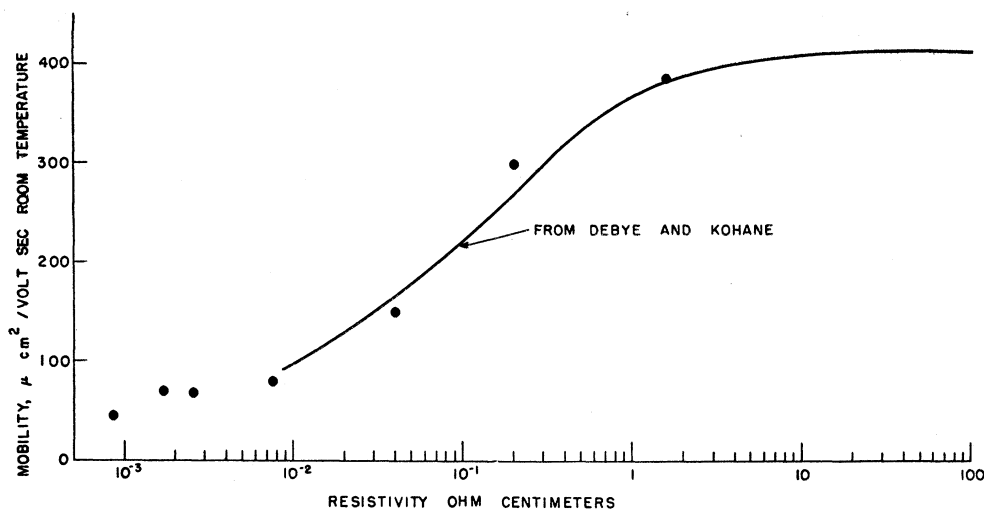


Fig. 3. Total mobility as a function of resistivity for boron-doped silicon at room temperature.

the sum of the change due to lattice contraction and the change due to substituting light boron atoms for silicon. This may be taken as reassurance that boron does, in fact, enter the silicon lattice substitutionally.

If one takes the equation for the net density change and calculates the anticipated change in density for lightly boron-doped silicon (points not included because of the scale used), it is found that the measured density increase is greater than anticipated. It is now recognized, however, that the data for these very lightly doped samples cannot be used in the argument since the density differences measured are of the same order or smaller than the variation ( $20 \times 10^{-6}$  density units) found between different crystals of silicon of presumably similar properties. Thus, the sensitivity of the method has been greater than necessary because of larger variations which were not controlled here. However, the fact that such readily measurable differences in density exist has naturally suggested further investigation.

#### ELECTRICAL PROPERTIES OF BORON-DOPED SILICON

The resistivity of bars of boron-doped silicon is given in Table III. The resistivity was measured potentiometrically using a moving probe. The linearity of the recorded traces of the potential drop as a function of probe position along the bars indicates good uniformity. The bars were cut transverse to the direction of crystal growth.

The number of silicon atoms/cc in pure silicon is readily calculated from the density as  $(2.3306/28.09) \times 6.024 \times 10^{23}$  or  $5 \times 10^{22}$  atoms/cc. Knowing that boron is substitutional in silicon, the number of boron atoms/cc is readily obtained from the composition given in atom percent. These numbers also appear in Table III. A mobility for holes may be calculated from the resistivity and number of carriers,  $N$ , assuming one carrier for each boron atom, since  $\mu = 1/Ne\rho$ . In

Fig. 3 these calculated room temperature mobilities are compared with the total mobility curves used and tested by Debye and Kohane.<sup>9</sup> This confirms the assumption of Pearson and Bardeen<sup>1</sup> that each substituted boron atom accepts an electron.

From the room temperature data it is not possible to determine the transition from semiconduction to metallic conduction. More information on the electrical properties is obtained from Hall coefficient vs temperature data.

#### SUMMARY

(1) The density of single-crystal silicon has been determined by a gradient density column technique as  $2.33067$  ( $25.3^\circ\text{C}$ ), a value found to agree with the density calculated from the x-ray determined lattice parameter  $5.4295 \pm 0.0005\text{\AA}$ .

(2) The lattice contraction and density of boron-doped silicon of chemically determined compositions was measured. The data are analyzed to show that boron enters the silicon crystal substitutionally.

(3) The above conclusions rest on the assumption that in a distorted crystal the number of atoms/cc

TABLE III. Room temperature electrical data for boron-doped silicon.

Sample	Atom percent boron	Carriers/cc <sup>a</sup>	$\rho$ ohm-cm <sup>b</sup>	$\mu\text{cm}^2/\text{volt sec calc.}$
RR-55	0.31 <sup>4</sup>	$1.5^5 \times 10^{20}$	$8.7 \times 10^{-4}$	46
RR-54	0.10 <sup>4</sup>	$5.2 \times 10^{19}$	$1.7 \times 10^{-3}$	71
RR-53	0.05 <sup>2</sup>	$2.6 \times 10^{19}$	$3.5 \times 10^{-3}$	69
RR-52	0.02 <sup>1</sup>	$1.0^5 \times 10^{19}$	$7.6 \times 10^{-3}$	78
RR-51	0.002 <sup>1</sup>	$1.0^5 \times 10^{18}$	$4.0 \times 10^{-2}$	149
RR-50	0.0002 <sup>1</sup>	$1.0^5 \times 10^{17}$	$2.0 \times 10^{-2}$	298
RR-49	0.00002 <sup>1</sup>	$1.0^5 \times 10^{16}$	1.55	384

<sup>a</sup> Calculated assuming one carrier per boron atom.

<sup>b</sup> Measured at  $25^\circ\text{C}$ .

<sup>9</sup> P. P. Debye and T. Kohane, Phys. Rev. **94**, 724 (1954).

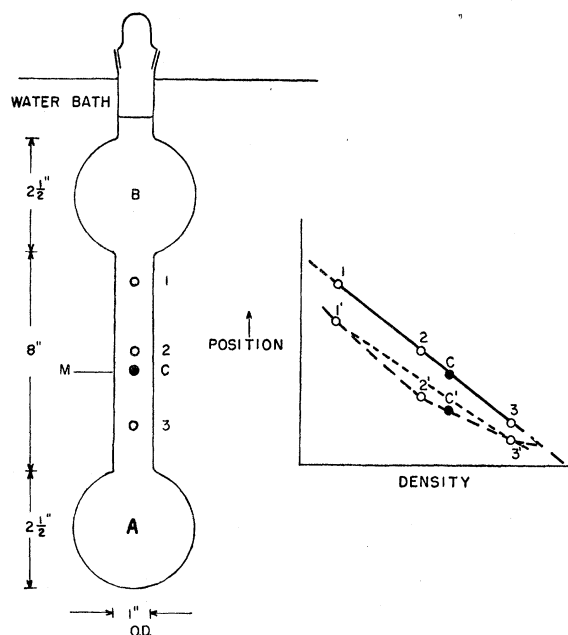


FIG. 4. Density gradient column and principle of interpolated density of unknown from bodies of calibrated density.

determined by x-rays is the same as the number of atoms/cc obtained from the density. This situation has been discussed by Eshelby.<sup>10</sup> We may alternatively assume in the present work that boron is substitutional and derive evidence for the validity of Eshelby's conclusions.

(4) The electrical resistivity at room temperature of boron-doped silicon shows each boron atom an acceptor of one electron and leads to hole mobilities consistent with previous theoretical and experimental results as given by Debye and Kohane.

#### ACKNOWLEDGMENTS

The zone melting and crystal preparation for these studies was performed by R. Riehl and P. Friguletto. Others whose help has been greatly appreciated particularly from discussion and interest and whom the author has not been able to acknowledge in the text have been E. A. Taft, L. Apker, M. H. Hebb, A. W. Overhauser, and H. Brooks.

#### APPENDIX. DENSITY GRADIENT METHOD

A precision density method particularly well suited to measuring small differences is the *density gradient method* developed by Linderstrom-Lang<sup>7</sup> to study the density change in liquids. Its adaptation to solids follows directly.

As may be seen in Fig. 4, the gradient column consists of two bulbs connected by a tube. The lower bulb, is filled to some middle mark, *M*, with a solution, *A*, whose density is greater than the objects being

studied. The remainder of the column is filled with a similar solution, *B*, adjusted to have a density less than the material investigated. The two liquids are gently stirred in the region, *M*, and the thermostated column allowed to stand in order that a stable gradient in density free from convection is set up from *A* to *B*. An object of density between that of solutions *A* and *B* when placed in the column will come to rest at some position at which its density is matched by that of the liquid mixture. In order to establish this density, the density distribution in the column must be known. Of several possible methods, the most straightforward is to introduce several objects of calibrated density. The density of the unknown is readily determined by interpolation from the positions of the calibrated bodies. It is obvious that the precision increases with more calibrated pieces in the column, particularly if these are of nearly the same density as the sample under study.

The density columns used were of the dimensions given in Fig. 4. With these dimensions, objects placed near the vertical axis of the column did not tend to move to the glass walls as readily as with columns of smaller tube diameter.

Many solutions cannot be used because of instability from moisture, air, or light. We successfully used solutions of iodobenzene [ $d=1.824(20^{\circ}\text{C}/4^{\circ}\text{C})$ ] with either diiodomethane [methylene iodide,  $d=3.325(20^{\circ}\text{C}/4^{\circ}\text{C})$ ] or 1,3-diiodopropane (tri-methylene diiodide,  $d=2.561(25^{\circ}\text{C})$ ). These liquids were obtained from Eastman Kodak Company and were filtered through fritted glass before use.

The density columns and solutions were maintained in a 94 gallon (American Instrument) glass-sided water bath controlled at  $25.3^{\circ}$  to  $\pm 0.001^{\circ}\text{C}$ .

Calibration spheres about  $\frac{1}{8}$  in. diameter were made from a glass rod produced by fusing two tapered rods of different density laid side by side. From such a glass "grade," spheres ranging in density from that of one glass to the other were readily melted and dropped from the rod. For these studies, Nonex ( $d=2.35$ ) and uranium ( $d=2.27$ ) glasses were used. [Corning 7720 and 3321 respectively.]

In order to avoid calibrating an unnecessarily large number of spheres, the glass spheres together with a piece of silicon were placed in a relatively insensitive column. Those spheres coming to rest close to the silicon were recovered for calibration. The density of the spheres selected for calibration was determined by making up solutions of the same liquids used in the column and of a composition that would just float them. The density of these solutions was then determined pycnometrically. The procedure is very laborious since the composition of the flotation solution must be such that finally one drop of added mixture not only floats the specimen but also represents a density change in the solution within the ultimate accuracy desired. These final adjustments were made with solutions

<sup>10</sup> J. D. Eshelby, J. Appl. Phys. **25**, 255 (1954).

of such density that a drop added to the calibrating solution represented a stepwise change of about  $5 \times 10^{-6}$  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 volumometer pycnometer calibrated with boiled distilled water.<sup>11</sup> The calibration is good to  $\pm 0.00001$  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  $310 \times 10^{-6}$  g/cc separated by about 10 cm in the column. The position of the specimens in the column was read on a cathetometer to  $\pm 0.1$  mm. The sensitivity of the method was therefore of the order  $3 \times 10^{-7}$  g/cc even though the densities are known on an absolute scale to only  $10^{-5}$  g/cc.

<sup>11</sup> N. E. Dorsey, *Properties of Ordinary Water* (Reinhold Publishers, New York, 1940), p. 200.

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<sub>3</sub>, 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.<sup>12</sup> 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.

<sup>12</sup> G. J. Gallagher and K. B. Blodgett (private communication).

## Properties of Ohmic Contacts to Cadmium Sulfide Single Crystals

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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:

### 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<sup>1</sup> 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

(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  $\sim 1$  amp/cm<sup>2</sup> 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  $\sim 10$  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.

were predicted some 15 years ago by Mott and Gurney,<sup>2</sup> 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<sup>3</sup> 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

<sup>2</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), pp. 168-173.

<sup>3</sup> A. Rose and R. W. Smith, *Phys. Rev.* **92**, 857 (1953).

<sup>1</sup> R. W. Smith and A. Rose, *Phys. Rev.* **92**, 857 (1953).