Space-Charge-Limited Currents in Single Crystals of Cadmium Sulfide*

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Currents as high as 20 amperes per cm^2 can be drawn through thin insulating crystals of CdS in the dark. A series of experiments demonstrate with a high degree of certainty that these are space-charge-limited currents—the solid state analog of space-charge-limited currents in a vacuum. This conclusion is contrary to a recently published interpretation of similar observations on CdS crystals by Böer and Kümmel.

The use of pulsed voltages made possible the observation of currents close to those of a trap-free solid. The steady-state currents are many orders of magnitude lower than these but still many orders of magnitude higher than would be expected from the low-field resistivity of the insulator. The presence of traps determines the form and magnitude of the steady-state current-voltage curves. Conversely, these curves become a sensitive tool for the measurement of trap densities. Trap densities computed independently from space-charge-limited currents and from photoconductive currents show reasonable agreement.

INTRODUCTION

THE early band theory models of an insulator carried with them implicitly the suggestion that if free carriers could be injected into either the conduction band or the valence band, these carriers could move freely through the solid. The magnitude of current that could be passed through a "perfect" insulator would be limited only by the space charge of the carriers themselves, just as the space-charge-limited currents in a vacuum diode. Mott and Gurney[1] derived the relation:

$$I=10^{-13}V^2\mu k/d^3 \text{ amperes/cm}^2 \qquad (1)$$

for the space-charge-limited current I through a slab of insulator d centimeters thick when V volts were applied. μ and k are the drift mobility and dielectric constant respectively. It is interesting that this expression leads to the expectation of some tens of amperes per square centimeter through an insulating sheet 10^{-3} cm thick when ten volts are applied across opposite faces.

The literature not only does not bear out these large currents but is almost devoid of any evidence for steady-state space-charge-limited currents. Gudden,[2] and many others since, have described the *transient* effects of space charge in insulators, chiefly in suppressing photo- or bombardment-induced currents. Weimer and Cope[3] cite evidence for small photogenerated space-charge-limited currents thin films of amorphous selenium. The currents were of the order of 10^{-7} ampere/cm^2, but they were nevertheless *steady* currents. The present work describes the evidence for large, steady space-charge-limited currents drawn through thin insulating crystals of CdS by means of ohmic contacts.[4]

EARLY OBSERVATIONS

The first observations that led to identifying the space-charge-limited currents are shown in Fig. 1 which represents the V-I characteristics as seen on an oscilloscope. Sixty-cycle/sec ac voltages up to about 100 volts were applied across a thin ($\sim 5\times10^{-3}$ cm) insulating CdS crystal having indium electrodes. With two different values of light on the crystal, the two linear characteristics F_1 and F_2 were obtained. With the crystal in the dark and a small ac voltage applied, the curve a_1 was obtained. (If the amplitude of ac voltage is held fixed, the turned up ends of the a_1 curve tend to settle towards the voltage axis.) If the amplitude of ac voltage is increased toward V_1,

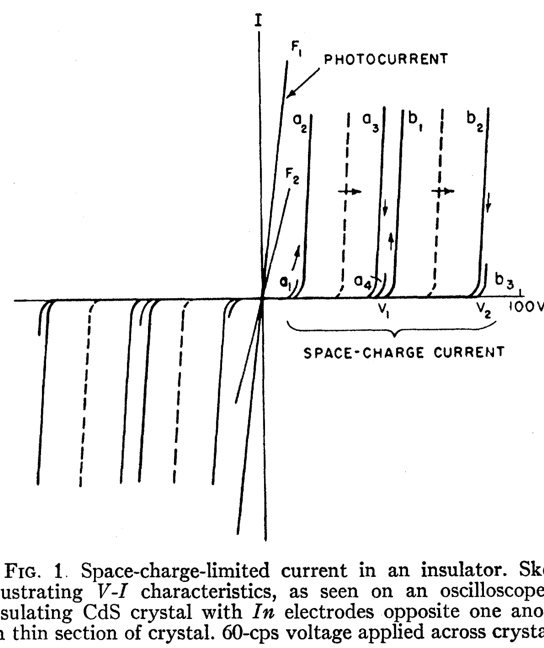

FIG. 1. Space-charge-limited current in an insulator. Sketch illustrating V-I characteristics, as seen on an oscilloscope, of insulating CdS crystal with *In* electrodes opposite one another on thin section of crystal. 60-cps voltage applied across crystal.

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

[2] B. Gudden, *Lichtelectrische Erscheinugen* (Verlag Julius Springer, Berlin, 1928).

[3] P. K. Weimer and A. D. Cope, RCA Rev. 12, 314 (1951).

[4] R. W. Smith, preceding paper [Phys. Rev. 97, 1525 (1955)].

the curve a_1 "shoots up" to the form a_2 and slides along the voltage axis with increasing amplitude of ac voltage. If the voltage amplitude is held fixed at V_1, the curve a_3 settles down to the form a_4.

At this point the amplitude of ac voltage may be reduced to zero and again increased toward V_1. Both during the decrease of voltage and during the increase of voltage the current remains vanishingly small until the voltage V_1 is reached at which point curve a_4 is retraced. Further increase of voltage from V_1 towards V_2 causes a_4 to "shoot up" again to b_1, slide along the voltage axis to b_2 and settle down to b_3 when the voltage amplitude is held fixed at V_2.

The interesting features of these V-I characteristics are the time dependence and the highly nonlinear but symmetric form of the curves.

The observation of a rapidly rising current-voltage curve is not in itself surprising. This is, indeed, a common observation in semiconductor measurements. And any one of several phenomena are commonly used to explain such curves. The phenomena include field emission from electrodes, from traps or from the valence band; collision ionization of trapped or valence electrons; poor contact; barriers; and heating effects. What *was* surprising was that none of these phenomena appeared to fit the observations.

The use of ohmic contacts[4,5] ruled out poor contacts and field emission from the electrodes. The linear current-voltage curve under illumination ruled out collision ionization. The low fields ($\sim 10^3$ volts/cm) ruled out field emission from traps or the valence band. The low currents ruled out heating effects. And finally, the assumption of internal barriers appeared improbable in the light of the otherwise regular performance of the crystal as a simple uniform photoconducting insulator.

In addition, the following effects were noteworthy: The high burst of current when the voltage was raised

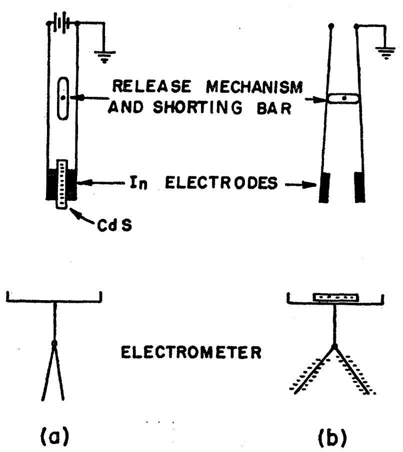

FIG. 2. Schematic drawing of experiment to measure charge injection in an insulator.

[5] C. I. Shulman (to be published).

followed by a steady decline in current on standing; the increased resistance at a given voltage resulting from the previous application of higher voltage; the symmetry of the curves on the voltage axis.

QUALITATIVE INTERPRETATION

A quick appraisal of the expected properties of space-charge-limited currents in a solid, as modified by the presence of traps, indicated that most of the observations could be qualitatively accounted for by the assumption of such currents. These currents were all the more reasonable because the metal contacts were ohmic—that is, the contacts provided a reservoir, or excess of carriers, ready to enter the crystal as needed. A qualitative description of the properties of space-charge-limited currents in a solid follows.

When a voltage is first applied across the crystal, space charge, in the form of free electrons from the cathode, is forced into the crystal via its conduction band. This free electron charge gives rise to a large burst of current. If the space charge remained in the conduction band, the peak value of the transient current would continue as a steady current. In actual crystals, however, one must take into account the effects of trap densities of the order of 10^{15} cm^{-3}. The free charge forced into the conduction band settles into the traps, more or less rapidly, the rate being determined by the capture cross section of the traps. This accounts for the transient increase in current and subsequent decrease on standing.

For a given voltage across the crystal a fixed amount of charge is forced into the crystal; most of this charge becomes trapped and only a small fraction remains free. Because the trap density is likely to be large compared with the density of space-charge electrons, one can take as a first approximation that all of the charge is condensed into traps. The condensation of electrons in traps raises the Fermi level towards the conduction band. To preserve a proper statistical equilibrium, the density of electrons in the conduction band must now be increased in accordance with this shift in Fermi level. The second approximation is then to allocate some of the condensed or trapped charge to the conduction band. These two steps usually give a fairly accurate approximation as suggested by the following numerical example. Let the applied voltage force 10^{13} electron charges per cm^3 into the crystal. Let this result in raising the Fermi level 0.1 volt towards the conduction band. If the crystal were an insulator having 10^6 free electrons/cm^3 prior to the application of a voltage, it will now have about 10^8 free electrons per cm^3 to be consistent with the new position of the Fermi level. These 10^8 free electrons taken out of the 10^{13} condensed electrons will obviously have a negligible effect on relocating the Fermi level.

If the traps are more or less uniformly distributed in energy in the forbidden zone, equal increments in voltage will make equal energy shifts in the position of the Fermi level. Since, however, the free electron density depends exponentially on the position of the Fermi level, the free electron density will increase exponentially with, or at least as some high power of, the applied voltage. This accounts for the observed high power dependence of current on voltage. By way of contrast, for a trap-free solid the current should increase only as the square of the applied voltage.

The space-charge-limited currents were also consistent with the observed low fields, there being no theoretical threshold field for the observation of space-charge-limited currents. Finally, it was reasonable to expect that, when the crystal was exposed to light, the density of photo-generated carriers would exceed the density of space-charge-injected carriers and that these photo-generated carriers would dominate the behavior of the crystal and lead to the ohmic behavior shown in Fig. 1.

DIRECT EVIDENCE OF SPACE-CHARGE

The interpretation in terms of space-charge-limited currents, with most of the space charge being trapped, suggested that one ought to be able to make a direct observation of this charge. Figure 2 shows the experimental arrangement used to make this test.

The crystal was held by spring action between two indium tipped electrodes. The crystal was mounted in a light-tight box and poised over a metal pan connected to an electrometer. Leads from the two electrodes were taken through the light-tight box to a source of voltage. One electrode was grounded. The other electrode could be connected to the positive or negative terminal of a dry cell or to ground. Finally, by an external mechanical arrangement the crystal could be released from the electrodes and dropped into the electrometer pan. The following observations were made:

(1) Both electrodes to the crystal were kept at ground and the crystal dropped into the electrometer pan. No charge was recorded. This indicated that the electrodes did not contribute any significant charge to the crystal by tribo-electric action.

(2) One electrode was grounded and the other electrode was held at *either* plus 100 volts or minus 100 volts relative to ground. A negative charge was recorded by the electrometer when the crystal was dropped into the pan. This test was subject to the criticism that charge from the electrodes might have in some way rubbed off onto the surface of the crystal. Hence the next test.

(3) One electrode was kept at ground. The other electrode was first tapped on the plus 100 volt terminal of the dry cell and then returned to ground, so that both electrodes were at ground just before the crystal was dropped to the electrometer pan. A negative charge was recorded. The same negative charge was recorded when the second electrode was tapped on the minus 100 volt terminal of a dry cell instead of the plus 100 volt terminal. The fact that the same negative charge was observed for either polarity of voltage applied to the crystal ruled out the possibility that the charge was due to a nonuniform resistance of the crystal. The internal charge would have changed sign in the latter instance.

(4) The magnitude of the charge was about half that expected from space-charge considerations and the geometry of the crystal. The uncertainty in area of contact of the electrodes could easily account for this discrepancy.

The procedure in item 3 was made possible by the fact that the space charge, forced into the crystal, was mostly trapped and remained in the crystal even when both electrodes were later grounded before the crystal was released.

DC CURRENT-VOLTAGE CURVES

Figure 3, curve I_0 shows an early measurement of the current through a crystal 5×10^{-3} cm thick when the crystal was kept in the dark. At each point the

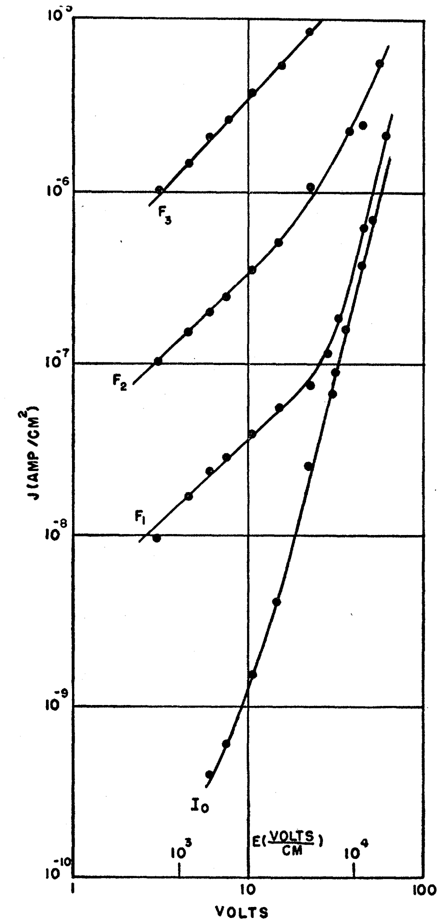

FIG. 3. Space-charge-limited current in an insulator. Dc measurement on a crystal similar to that of Fig. 2. I_0 is dark current curve and F_1, F_2, and F_3 are curves with increasing irradiation.

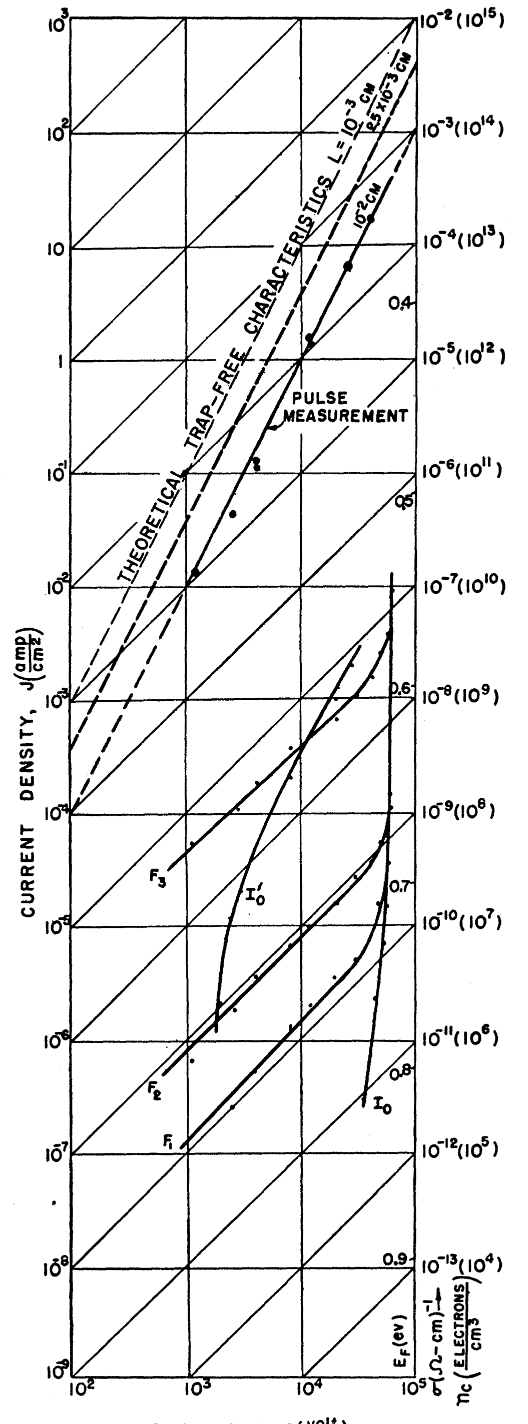

FIG. 4. Space-charge-limited current in an insulator. I_0' initial dark current curve after exposure to light, I_0 thermal equilibrium dark current curve. F_1, F_2, and F_3 curves obtained with different light levels on the crystal. The conductivity, density of carriers in conduction band n_c, and theoretical square-law curves calculated on basis of mobility $\mu=100$ and dielectric constant $k=10$ for CdS.

current was allowed to settle down to a reasonably stationary value. In the light of later experience it is not certain that sufficient time was allowed to get accurately stationary values. The curve, nevertheless, shows the high power dependence of current on voltage. In this case the current increases approximately as the fourth power of the voltage.

Also in Fig. 3 are shown curves marked F_1, F_2, and F_3. These curves were taken with small amounts of light on the crystal, the light intensity increasing from F_1 to F_3. They are significant in showing that for the same fields at which the dark current is increasing as the fourth power of the voltage, the photoconductive current increases only as the first power. These curves support the argument that the high power dependence of the dark current cannot be ascribed to collision ionization processes. It is also evident from Fig. 3, that at higher light intensities the transition from ohmic behavior to space-charge-limited current behavior occurs at higher voltages. This is consistent with the argument that the behavior is either ohmic or space-charge-limited depending on whether the volume generated carrier density or the injected carrier density predominates.

Figure 4 shows perhaps the most significant set of curves taken on a single crystal. The crystal thickness was 2.5×10^{-3} cm; the electrode area 5×10^{-4} cm^2. Again, the curve marked I_0 represents the current through the crystal in the dark. This time, however, sufficient time was allowed for the current to come to a reliably stationary value at each voltage. At the low current end, the time required was of the order of hours. The current increases as almost the 20th power of the voltage. Such a dependence[6] would be expected from traps uniformly distributed in energy at least in the range of 0.55 to 0.8 volt below the conduction band. This is the range of Fermi levels appropriate to the range of conductivities covered by curve I_0. It is also to be noted from this curve that the dark conductivity at fields below 10^4 volts/cm is well below 10^{-12} (ohm-cm)$^{-1}$.

The curves F_1, F_2, and F_3 were taken with the crystal exposed to increasing amounts of steady light. They show again, as in Fig. 3, the ohmic behavior obtained when the volume generated carriers exceed the space-charge injected carriers. They offer additional evidence that the electric fields (10^3 to almost 10^5 volts/cm) are not sufficient to cause collision ionization or even to significantly alter the "electron temperature."

TIME DEPENDENT CURRENTS

The curve I_0' of Fig. 4 has an important bearing not only on the interpretation of the present work but also on the interpretation of similar data reported by Böer.[7] Curve I_0' was taken with the crystal in darkness,

[6] A. Rose, following paper [Phys. Rev. 97, 1538 (1955)].
[7] K. W. Böer and U. Kümmel, Z. Naturforsch. 9a, 177 (1954).

but within a few minutes after it had been exposed to room light. Its particular shape is not to be emphasized since that depends on how rapidly the curve is taken. What is to be emphasized is that the I_0' curve lies well above the I_0 curve and that the I_0' curve represents a higher than ohmic dependence of current on voltage. A further significant fact is that if one waited long enough in taking this data, each point on the I_0' curve would have settled down to the I_0 curve.

The I_0' curve may be understood as follows. After the crystal has been exposed to room light and is put in darkness, thermal equilibrium is not immediately established. The conductivity decays roughly as t^{-1} and so decays more slowly as the conductivity decreases.[8,9] During this decay process many of the higher-lying trapping states are filled. A short-hand way of describing the electron distribution is to say that the steady-state Fermi level[10] is closer to the conduction band than its final equilibrium position.[9] Under these circumstances, the space-charge electrons are injected through the conduction band into levels closer to the conduction band so that a larger fraction of the electrons remain free. This accounts for the currents of the I_0' curve being higher than those of the I_0 curve. In the final steady state condition, the currents and electron distribution of the I_0' curve settle down into those of the I_0 curve. This settling process which would occur in the dark with no voltage applied to the crystal is considerably hastened by application of a voltage since the rate of approaching equilibrium is proportional to the free electron density. It is this hastening of the decay that accounts in large part for the ac observation described at the beginning of this paper, namely, the increase in resistance at a given voltage resulting from the previous application of a higher voltage. Curve I_0' was taken rapidly with increasing voltages. When the voltage range is retraced from high to low voltages a curve is obtained lying considerably below I_0' and close to I_0.

The last statement describes also the character of current-voltage curves reported by Böer for CdS crystals. Böer's interpretation is diametrically opposed to that taken here. He states that the high currents of the I_0' curve are a result of the emptying of traps by the applied field, either through collision ionization or field emission from traps; in brief, a field-induced "glow curve." What is common to both interpretations, Böer's and ours, is that the crystal after exposure to light, is left in a nonequilibrium condition and that, to approach equilibrium, electrons must recombine with deep-lying trapped holes created by previous optical excitation. In Böer's interpretation the electrons that recombine with the deep-lying holes come from higher-lying states and must first be excited into the conduction band by the applied field before recombining. While they are in the conduction band they would account for the excess currents of curve I_0'. As they drop into the deep-lying holes, the curve I_0 would be approached.

Our interpretation is that up to fields of about 5×10^4 volts/cm, the field is not strong enough to excite electrons from high-lying states into the conduction band. The electrons that recombine with the deep-lying holes are those that are injected into the conduction band from the cathode. The injection into the conduction band provides the initially high currents. The recombination of conduction electrons with deep-lying holes accounts for the approach to the low currents of curve I_0. The approach to I_0 is accelerated by the increased density of conduction electrons injected by the applied field. This approach takes place even in the absence of an applied field but much more slowly consistent with the low density of conduction electrons. The chief evidence for the present interpretation in terms of space-charge-limited currents is the fact that the electric fields are too low to extract electrons from or to ionize traps. Evidence of nearly equal importance, however, is contained in the curve marked "pulse measurement" in Fig. 4.

Pulse Measurements

Since space charge is injected first into the conduction band and *then* becomes largely trapped, one might expect to see the high theoretical currents characteristic of a trap-free solid if one looked fast enough after applying a voltage. Such a measurement was made using a voltage pulser[11] and an oscilloscope. Currents several orders of magnitude higher than those of curve I_0 were observed but they still fell far short of the theoretical curves shown in Fig. 4, both in magnitude and form. Since the oscilloscope could not resolve time better than about 100 microseconds, it was felt that some of the charge might be trapped before one could see its contribution to the pulsed current.

It was found, however, that if a small amount of steady bias light were used, much higher values of pulsed current could be observed. The curve marked "pulse measurement" in Fig. 4 was taken in this way. Two characteristics of this curve are immediately striking. The magnitudes of the currents are close to the theoretical values for a trap-free solid computed from Eq. (1), using a mobility of 100 cm²/volt sec. Especially at the lower fields these currents are well over 8 powers of ten higher than those of curve I_0. At the high end, the current densities reach 20 amperes/cm². The second significant characteristic is that the shape of this curve quite accurately follows the square-

[8] R. W. Smith, RCA Rev. **12**, 350 (1951).
[9] A. Rose, RCA Rev. **12**, 362 (1951).
[10] The steady-state Fermi level is defined by the relation $n=N_c\exp(-E_f/kT)$, where n is the density of free electrons, N_c is normally about 10^{19} at room temperature, and E_f is the energy difference between the bottom of the conduction band and the steady-state Fermi level.

[11] We are indebted to Dr. L. S. Nergaard for the use of this pulser which he had designed for use in oxide cathode work.

law dependence on voltage required by Eq. (1). Not only does the curve satisfy the magnitude and form of space-charge-limited currents in a trap free solid but it implies also two other important conclusions. The accurate square-law dependence on voltage means that in this range of fields, up to 5×10^4 volts/cm, the mobility is not field-dependent. The electron temperature does not depart significantly from the crystal temperature. Also, for currents up to 20 amperes/cm^2 the indium contacts are still ohmic, that is, they still supply a reservoir or excess of electrons at the metal-insulator interface. This must mean that the Fermi level of the indium metal is within about three-tenths of a volt of the conduction band of the CdS crystal.

Traces of the transient currents obtained with pulsed voltages are shown in Fig. 5. The decay time for these currents is of the order of a millisecond. This is also the decay time observed at high light intensities for photocurrents in this same crystal. The traps into which the space-charge electrons and the photoelectrons decay are either the same or at least have the same capture cross section. This cross section was computed from the relation $s=(\tau vn)^{-1}$ cm^2 to be 10^{-19} cm^2. τ is the decay time, 10^{-3} second; v the thermal velocity of an electron, 10^7 cm/sec; and n is an estimate of the *total* number of traps into which electrons may decay, 10^{15}/cm^3.

TEMPERATURE DEPENDENCE

The injection of space-charge electrons into an insulator transforms it into a semiconductor of increasing conductivity as the voltage is increased. At any given voltage the current should vary with temperature in a similar fashion as for any semiconductor having a conductivity of the same order of magnitude. The total space-charge in the crystal should not vary with temperature; but the fraction of space-charge that is free should in general increase exponentially with increasing temperature. In reference 6 the following relation was obtained to describe the effect of temperature on the form of the current-voltage curve:

$$I \propto V^{(T_c/T)+1}.$$

T_c is a characteristic temperature describing the distribution of traps in energy. Small values of T_c are

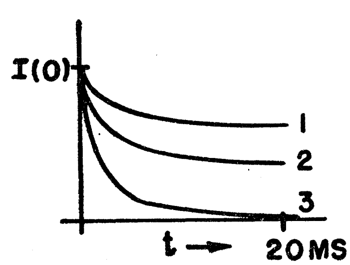

FIG. 5. Current in CdS crystal due to square voltage pulses of 20-millisecond duration. Curves 1, 2, and 3 correspond to initial currents I_0 of 6×10^{-6}, 2×10^{-5}, and 3×10^{-3} amp respectively.

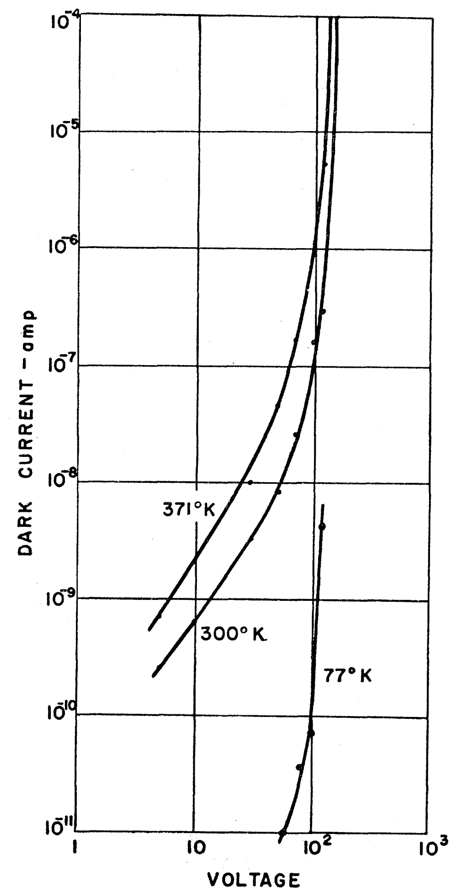

FIG. 6. Space-charge-limited current in CdS as a function of temperature.

associated with trap distributions varying rapidly with energy, while large values of T_c approximate a slowly varying trap distribution. From Eq. (2), one would expect a steeper current voltage curve at lower temperatures. Figure 6 shows three current-voltage curves taken at different temperatures. Qualitatively the currents are smaller for lower temperatures, and the curves steeper at lower temperatures in accordance with the expected behavior. Quantitatively, the ratio of currents between the 371°K and the 300°K curves are of the right order. The currents of the 77°K curve should be much lower. It is possible that the electron distribution in the crystal did not come into thermal equilibrium with the crystal temperature. At these low carrier densities, approach to thermal equilibrium may easily require hours or days.

COMPARISON OF SPACE-CHARGE-LIMITED CURRENT WITH PHOTOCONDUCTIVE CURRENT

The energy distribution of traps determines the form of the current-light curve in photoconductivity measurements and also the speed of response. The energy distribution of traps also determines the form and magnitude of the space-charge-limited current-voltage curves. Conversely, from the observed curve forms and speeds of response one should be able to obtain the energy distribution of traps. A pertinent question is whether the trap distribution determined in the same crystal by the two independent methods of space-charge-limited currents and photoconductive currents shows any self consistency. Table I summarizes the appropriate relations derived in references 6 and 9.

In the limit for large values of T_c, the trap distribution becomes uniform in energy, the space-charge-limited current increases exponentially with voltage and the photocurrent increases linearly with light intensity. Figure 4 shows the exponential dependence of space-charge-limited current on voltage. Figure 7 shows the linear dependence of photo current on light intensity. Both sets of data were taken on the same crystal through the same electrodes. Both sets of data are consistent with a uniform or near uniform energy distribution of traps in the range of 0.5 to 0.8 ev below the conduction band.

The trap density computed from the space-charge-limited curve I_0 of Fig. 4 was 5×10^{12} traps/cm^3 in an energy range of kT at 0.7 volt below the conduction band. From photoconductivity measurements at the light levels of curves F_1 and F_2 of Fig. 4, the trap density was computed to be 0.5×10^{12}/cm^3 per kT at the same depth below the conduction band. Of the two estimates the space-charge-limited computation is likely to be the more reliable since the character or capture cross sections of the traps do not enter in. In the photoconductivity measurement, only those traps are measured from which thermal excitation occurs rapidly enough to keep pace with the decaying photocurrent (see reference 9).

TABLE I. The energy distribution and density of traps derived from data on photoconductivity and from data on space-charge-limited currents.[a]

	Space-charge-limited currents	Photoconductivity
Form of current curve	$I\propto V^{(T_c/T)+1}$	$I\propto F^{T_c/(T+T_c)}$
Trap density in range of kT near the Fermi level	$\frac{\Delta Q}{e}$	$\frac{\tau_0}{\tau}n_c$

[a] Notes: T_c defines the trap distribution in the relation $n_t\propto\exp(-E/kT_c)$, where n_t is the trap density at E volts below the conduction band. F is the number of optical excitations per second. ΔQ is the space charge forced into the crystal when the voltage is increased by an amount sufficient to double the current. τ_0 is the observed speed of response of the photoconductor. τ is the lifetime of a free carrier in the conduction band. n_c is the density of free carriers at which τ_0 is measured.

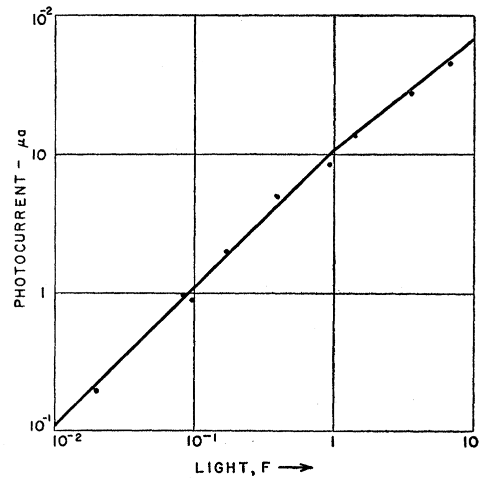

FIG. 7. Photocurrent-light (F) characteristic of CdS crystal.

The time of response at F_1 was 50 seconds and at F_2 was 6.6 seconds. At high light intensities the time of response leveled off at a value of 10^{-3} second, which should be close to the true lifetime of a carrier in the conduction band.

CONCLUDING REMARKS

Currents far in excess of ohmic currents have been measured through thin insulating crystals of CdS in the dark. A set of experiments has been described that identify these currents as space-charge-limited currents in a solid. These experiments include the direct measurement of the space charge; the matching of the form and magnitude of the theoretically expected current in a trap-free solid by using pulsed voltages; the analysis of the much lower steady-state currents in terms of a trap distribution that is consistent with independent photoconductivity measurements; and the confirmation that these currents can be obtained at fields too low to cause collision ionization or field emission from traps. The fact that the steady-state space-charge-limited currents are more than eight powers of ten lower than those in a trap-free solid (Fig. 4) is evidence that space-charge-limited currents represent one of the most sensitive tools for measuring the presence of traps, especially in those insulating crystals that approach a high degree of perfection.