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SPACE-CHARGE-LIMITED CURRENTS AS A TECHNIQUE FOR THE STUDY OF IMPERFECTIONS IN PURE CRYSTALS

M. A. LAMPERT, A. ROSE and R. W. SMITH
RCA Laboratories, Princeton, New Jersey

BY sweeping the Fermi level through the forbidden gap a great deal of information can be obtained about localized defect states in a crystal. The *minimum possible* departure from thermodynamic equilibrium is achieved if the position of the SSFL (steady-state Fermi level) is controlled through manipulation of a *single* type of carrier, namely through the voltage-controlled injection of excess carriers of one sign of charge. So long as the applied field does not substantially alter the velocity distribution of the free carriers, *all* states in the forbidden gap remain, under steady-state conditions, in normal thermal contact with the free carriers. For this reason, *all* localized states in the forbidden gap are "felt out" by the SCLC (space-charge-limited current).

The usefulness of the SCLC technique for obtaining data on imperfections is forcefully illustrated by recent measurements on single crystals of CdS. An experimental current–voltage curve* is shown in Fig. 1. As we shall see later, these measurements correspond to a situation where a set of defect states at a single, discrete energy level E_t dominates the nearby energy region in the forbidden gap, and further where the defect level lies above the thermal-equilibrium Fermi level $\bar{E}_F$. This situation is illustrated by an energy-band diagram in Fig. 2. E_c and E_v are the conduction-band minimum and valence-band maximum energy levels respectively. E_F is the steady-state electron† Fermi level, defined with respect to the free electron density is in the usual manner through the relation: $n = N_c \exp[(E_F - E_c)/kT]$ with N_c the effective density of states in the conduction band. At thermal equilibrium E_F coincides with $\bar{E}_F$.

In order to interpret and make use of the experimental curve of Fig. 1 we shall first examine the general structure of the J–V (current density–voltage) characteristic to be expected theoretically from a crystal with the energy-level configuration shown in Fig. 2. This J–V characteristic is the solid curve ABCDE, shown on a log–log plot, in Fig. 2. Its structure may be readily understood by following the motion of the Fermi level E_F through the forbidden gap as a function of applied voltage.

(1) At low voltages there is negligible injection of excess charge into the crystal (no significant departure of E_F from $\bar{E}_F$) and Ohm's law is observed (portion AB of the J–V curve).

(2) SCL current sets in at that voltage V_{TR} at which the density of *excess* free carriers equals $\bar{n}$, the thermal-equilibrium density, i.e. $n = 2\bar{n}$ and correspondingly $n_t = 2\bar{n}_t$, with n_t and $\bar{n}_t$ the trapped carrier density under

* This work was reported on at the Chicago meeting of the APS, March 1958. See SMITH R. W. *Bull. Amer. Phys. Soc.* II **3**, 129 (1958).

† We are concerned throughout this article with one-carrier currents. For the sake of definiteness we assume that the carriers are electrons.

voltage and at no voltage respectively. This corresponds to a departure of E_F from E_F^* by approximately kT. For a plane-parallel geometry and for $\bar{n}_t \gg \bar{n}$, $V_{TR} = ea^2\bar{n}_t/2\epsilon$ (m.k.s. units)[3], with e the electronic charge, ϵ the static dielectric constant, and a the cathode–anode spacing.

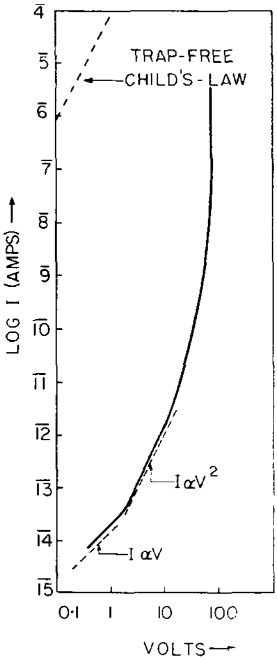

Fig. 1. Experimental current–voltage characteristic (solid line) for a single crystal of CdS. The cathode–anode spacing $a = 1{\cdot}7 \times 10^{-3}$ cm and the electrode area $\simeq 3{\cdot}5 \times 10^{-3}$ cm². The dashed lines indicate linear and square-law slopes respectively. The stippled curve is the (hypothetical) trap-free Child's law current for the same crystal.

(3) With further increase of voltage beyond V_{TR} additional excess charge is injected into the crystal and accordingly the Fermi level E_F moves closer to the conduction band. So long as E_F remains below E_t the ratio of free to trapped carriers, n/n_t, is a constant independent of voltage. It follows directly from this[2] that $J \propto V^2$ in this voltage range (portion B to C of the J–V curve).

(4) After the Fermi level E_F passes through the defect level E_t the current J rises steeply, but reversibly, with voltage (portion CD of the J–V curve). This sharp rise occurs[3] at the voltage $V_{TFL} = ea^2N_t/2\epsilon$, corresponding to complete filling of the defect states of density N_t. For $V < V_{TFL}$ excess charge is held almost exclusively in the defect states. After saturation of the defect states additional excess charge must appear in the conduction band. Thus, comparing the SCLC at voltage $2V_{TFL}$ with that at voltage V_{TFL}, $J(2V_{TFL})/J(V_{TFL}) \simeq (N_t/N_c)$

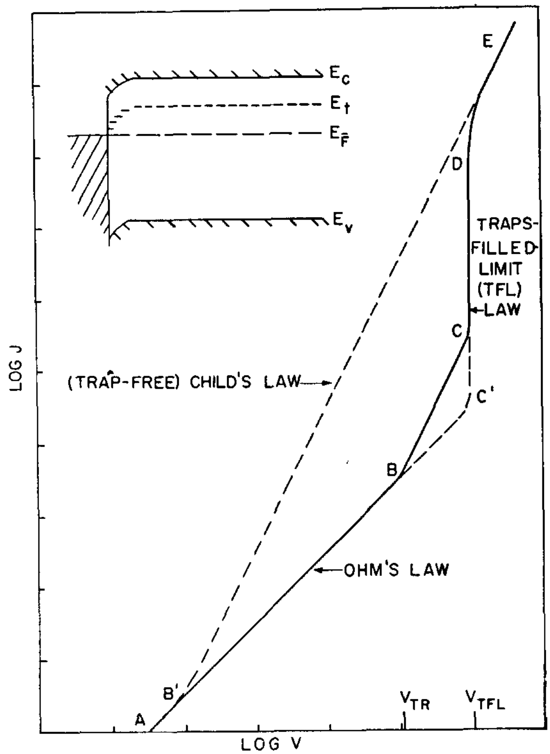

Fig. 2. Theoretical current density–voltage characteristic for a solid with plane-parallel geometry. The solid curve ABCDE refers to the case where the (dominant) traps lie at a single, discrete energy-level E_t lying above the thermal-equilibrium Fermi level E_F^*, illustrated by the accompanying energy-band diagram. If $E_t \lesssim E_F^*$, then a curve such as AC′DE would be expected. If there were no traps the curve AB′E would be expected.

$\exp[(E_c - E_t)/kT]$. At $T = 300°$K, $N_c \approx 10^{19}$ cm^{-3}. Taking $N_t = 10^{14}$ cm^{-3} and $E_c - E_t = 0{\cdot}4$ eV, this current ratio is about 100.

(5) For $V > 2V_{TFL}$, the excess free charge dominates the excess trapped charge so that the current–voltage characteristic coincides with that for a trap-free solid, namely the Child's (square) law of Fig. 2.

What information is obtained from measurement of a J–V characteristic such as curve ABCDE of Fig. 2? The crucial elements are the "vertical" rise CD and the square-law portion BC preceding it. The latter portion guarantees that the defect energy level lies above the thermal-equilibrium Fermi level, $E_t > E_F^*$, and therefore that the defect states are practically all empty at the outset. Knowing this, we obtain the density of defect states from the voltage at the "vertical" rise in current: $N_t = 2\epsilon V_{TFL}/ea^2$ (m.k.s.). A remarkable feature of this density determination is that it does not require any knowledge of basic transport quantities of the crystal, such as the effective mass m^* or mobility μ of the carriers. Consequently the error in measurement should be considerably less than a factor of two—which corresponds to unusually high accuracy in the current state of the art. The minimum defect density, $N_{t,min}$, that can be measured depends on the energy location E_t and the temperature. Thus, at 300°K, if $E_c - E_t = 0{\cdot}80$ eV then $N_{t,min} \approx 10^6$ cm^{-3} whereas if $E_c - E_t = 0{\cdot}40$ eV then $N_{t,min} \approx 10^{13}$ cm^{-3}.

Further information from SCLC measurements is contingent upon knowledge of transport quantities. Thus, the J–V characteristic in the square-law region preceding the vertical rise, segment BC of Fig. 2, can be explicitly written:[2]

$$J = \frac{2{\cdot}4\times 10^6}{gN_t}\left\{\exp\frac{(E_t - E_c)}{kT}\right\}\times \times K\mu\left(\frac{m^*_{ds}}{m}\right)^{3/2}\frac{V^2}{a^3}\,\mathrm{A/cm^2}$$

where all quantities are expressed in practical units and $T = 300$°K. Here K is the relative static dielectric constant and m^*_{ds} is the density-of-states effective mass. If g, m^*_{ds}/m and μ are all known, then $E_c - E_t$ is determined from the measured current in the square-law range BC of Fig. 2. Uncertainties in these quantities are reflected in a corresponding error in $E_c - E_t$. If $E_c - E_t$ is known from other measurements then the measured square-law current, portion BC of Fig. 2, yields a determination of the product $(\mu/g)(m^*_{ds}/m)^{\frac{3}{2}}$.

If no square-law portion is observed *preceding* the vertical rise, that is, if a J–V curve of type AC′DE of Fig. 2 is obtained, then accordingly less information is obtained from the SCLC measurement. In this case the effective defect states lie energetically at or below the Fermi level E_F and the vertical rise determines only the density of holes in the defect states at thermal equilibrium.

Applying the foregoing theory it is clear that the experimental current–voltage curve of Fig. 1, for a single crystal of CdS, is characteristic of a discrete defect level lying above the Fermi level E_F. The vertical portion yields a defect density of 3×10^{14} cm^{-3}. The square-law portion yields a defect energy level $E_c - E_t = 0{\cdot}8$ eV, taking $g = 2$, $\mu = 100$ cm^2/V-sec and $m^*_{ds}/m = 1/4$. Uncertainties in the latter quantities produce an uncertainty in $E_c - E_t$ probably not exceeding $2kT = 0{\cdot}05$ eV.

This report has been confined to discussion of *steady-state* SCL current measurements. Further information can be obtained by additional measurements of *transient* SCL currents in the same crystal on which steady-state measurements have been made. Thus the measurement of current decay can yield the capture cross-section of the defect center for free electrons. Also, recent theoretical and experimental studies (as yet unpublished) have revealed an intimate connection between SCL currents and photoconductivity. Consequently, the combination of SCLC and photoconductivity measurements provides a powerful means to disentangle kinetically occupied (recombination) centers from thermally occupied (trapping) centers. For example, photoconductive measurements on the CdS crystal responsible for the J–V characteristic of Fig. 1 have established unambiguously that the defect centers associated with the vertical rise do not function as electron traps under photo-excitation of the crystal, but rather have a kinetically-determined occupancy and must therefore be associated with recombination centers.

Further details on the theory of SCLC in solids are contained in references 1–3. Earlier experimental work is reported in reference 4.

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