ACKNOWLEDGMENTS

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Transfer of Electric Charges through Rutile Single Crystals*

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Electron transfer and onset of field emission has been investigated in TiO_2 single crystals with dc current-time characteristics parallel and perpendicular to the optic axis as function of voltage, temperature, electrode material, and light absorption. The currents are much larger and field emission sets in at lower voltage when the field is parallel to the optic axis. Higher temperature favors the current transfer by increasing the carrier mobility. The effect of different electrode materials proved minor, except in the case of Ti, which as cathode raised the current by about one order of magnitude. Photoelectric measurements showed that, in the critical voltage region of incipient field emission, light absorption can apparently force the current reversibly into the field-emitting stage.

THE PROBLEM

THE transfer of electrons through alkali halide crystals has been studied in the Laboratory for Insulation Research in some detail by a novel use of *F*-center discoloration.[1,2] Additively colored crystals can be described as electrons frozen into a positive matrix. The electrons may be mobilized by light absorption and moved toward the anode in a dc field. If they are discharged at the anode but not replaced from the cathode, a cathode fall builds up in an adjustable manner. When the field gradient at the cathode becomes high enough to enforce field emission, permanent currents can be drawn as long as the incident light keeps the electrons mobilized throughout the crystal. By observing these electronic currents as function of time, with voltage, temperature, and crystal treatment as adjustable parameters, much can be learned about field emission into dielectrics.

This work can be extended to crystals in which the electron transfer does not require optical activation. In TiO_2, for example, electrons move relatively freely, once mobilized by reduction or light absorption.[3] At the same time rutile offers strong anisotropy and high dielectric constant, two features of great interest for field-emission studies. The present investigation reports on the dc current transfer through rutile single crystals

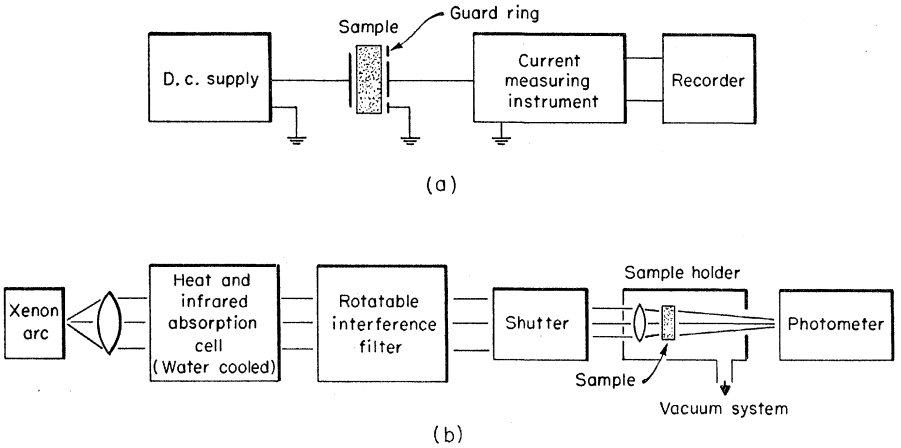

FIG. 1. Schematic diagram of measuring equipment: (a) electrical system; (b) optical system.

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[1] A. von Hippel, E. P. Gross, J. G. Jelatis, and M. Geller, Phys. Rev. **91**, 568 (1953).
[2] M. Geller, Phys. Rev. **101**, 1685 (1956).
[3] D. C. Cronemeyer, Phys. Rev. **87**, 876 (1952).

as function of time, temperature, voltage, orientation, and electrode material.

SAMPLES AND MEASUREMENT TECHNIQUE

Planes, cut from rutile boules of the National Lead Company, were oriented parallel and perpendicular to the optic axis, polished, cleaned by boiling in *aqua regia*, washed in warm KOH solution, rinsed in distilled water and steam, and dried at 125°C.[4] Three-terminal electrodes of various metals (Al, Ag, Au, Ca, Ni, Pt, or Ti) were deposited by evaporation. For room-temperature measurements, silver or platinum paint or an indium-gallium alloy was also used on occasion. In evaporating reactive metals, such as Al, Ca, and Ti, special care was taken to intercept the initial part of the metal as a getter and to protect the electrode against subsequent oxidation by an overlay of evaporated gold. Tin oxide electrodes served for some of the photoconductivity measurements because they are transparent in the wavelength range in question.

Figure 1 gives a schematic survey of the experimental setup, and Fig. 2 shows the sample holder, a modified version of that used previously by Geller.[2]

A vibrating-reed electrometer covered the range from 5×10^{-13} to 3×10^{-4} amp; an electrometer-type dc amplifier served for larger currents. Up to 3600 volts, the voltage was supplied by dry cells in grounded shield, for higher potentials by an electronic power supply.

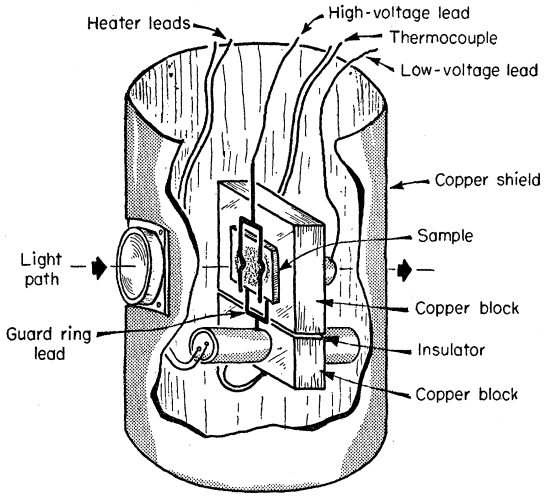

FIG. 2. Details of sample holder.

RESULTS

Figure 3 shows the current at 25°C for various voltages, measured with evaporated gold electrodes. In accord with Cronemeyer's conductivity measurements,[3] the currents drawn parallel to the axis are orders of magnitude larger than those perpendicular to it. At

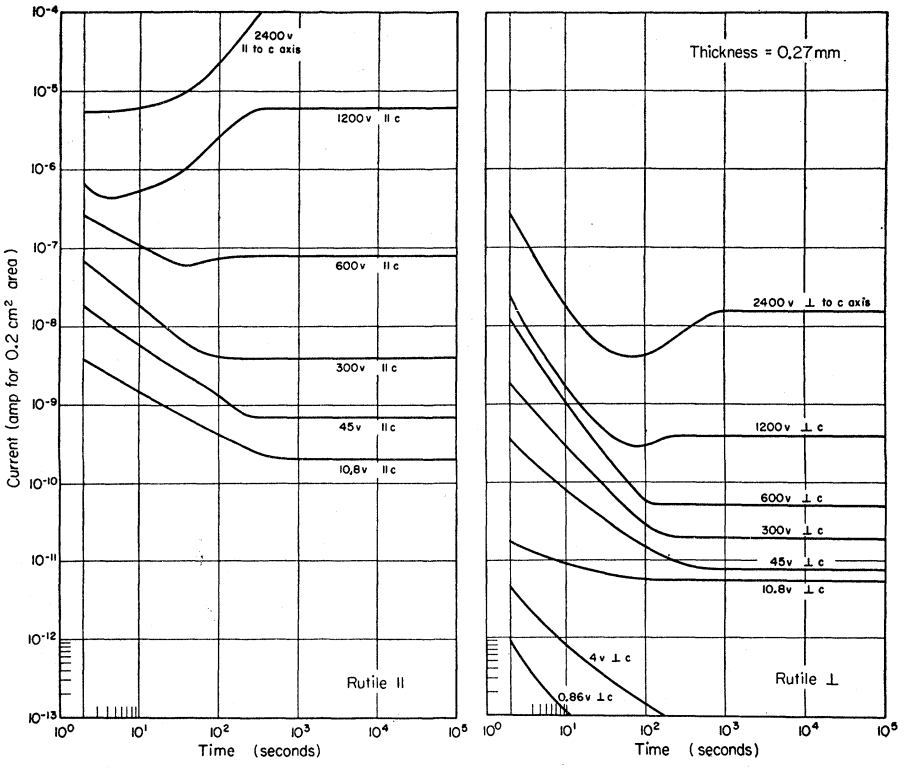

FIG. 3. Direct-current currents through rutile at 25°C ∥ and ⊥ to axis as function of time for various voltages.

[4] See also K. G. Srivastava, preceding paper [Phys. Rev. **119**, 516 (1960)].

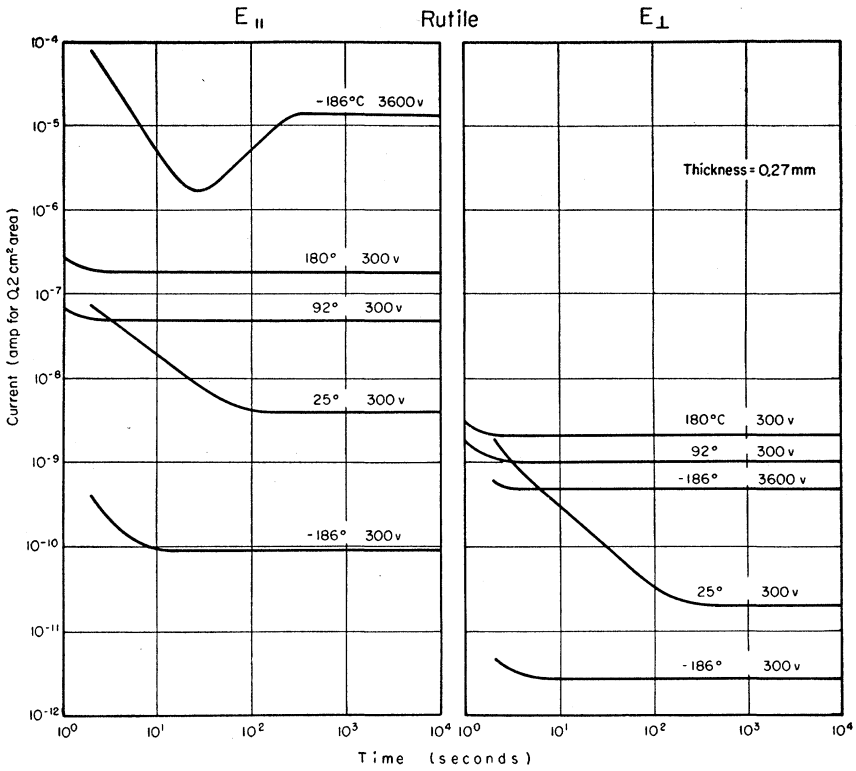

FIG. 4. Direct-current currents through rutile || and ⊥ to axis as function of time at various temperatures.

the lowest voltage (perpendicular) the current decays without stabilization, otherwise a definite leveling off to finite transconductance takes place.

In comparison to KBr,[1,2] the conductivity of TiO_2 is appreciably higher and, as the final currents indicate, field emission sets in much more easily. At 2400 volts parallel to the axis the current flow becomes so large that the heat input prevents stabilization.

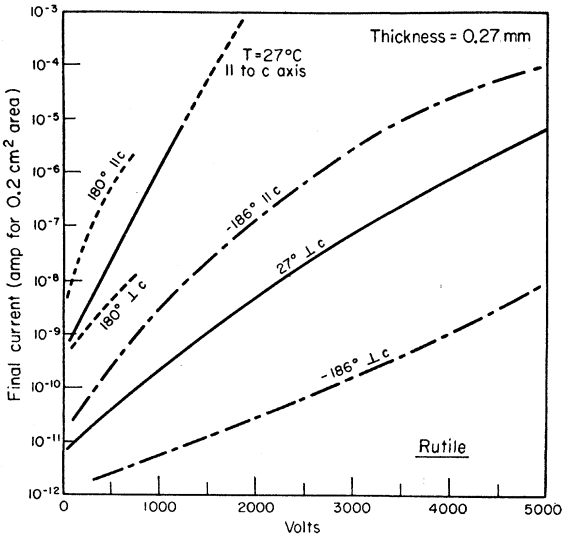

FIG. 5. Steady-state currents through rutile || and ⊥ to axis as function of voltage at various temperatures.

For the alkali halides, temperature has a minor effect on the final currents because the electrons are kept mobilized by light absorption. In TiO_2 the transconductance depends on thermal activation; hence, we expect and find that at −186°C the final currents are appreciably reduced (Fig. 4), while at +90°C and at +180°C they are strongly increased and simultaneously reach saturation faster. Obviously, the build-up of the field distortion that precedes field emission proceeds much more rapidly. The steady-state currents are summarized in Fig. 5.

The measurements shown in Figs. 3 and 4 are virgin characteristics: Between each step-up of the voltage the crystal is discharged and thus restored to its original condition. Figure 6 shows a set of such short-circuit characteristics. The space-charge polarization increases with applied voltage; its discharge proceeds more rapidly || than ⊥ to the axis and is speeded up at higher temperatures.

The measurements shown thus far refer to crystal plates of 0.27-mm thickness. In increasing the thickness to 0.49 mm, the final currents for equal voltage are reduced approximately by an order of magnitude (Fig. 7). This great field-strength sensitivity is in keeping with the field-emission situation.

If the current through the crystal, and with it the voltage drop between cathode and guard ring, becomes too high, surface discharges will develop from the cathode, acting now as anode against the guard elec-

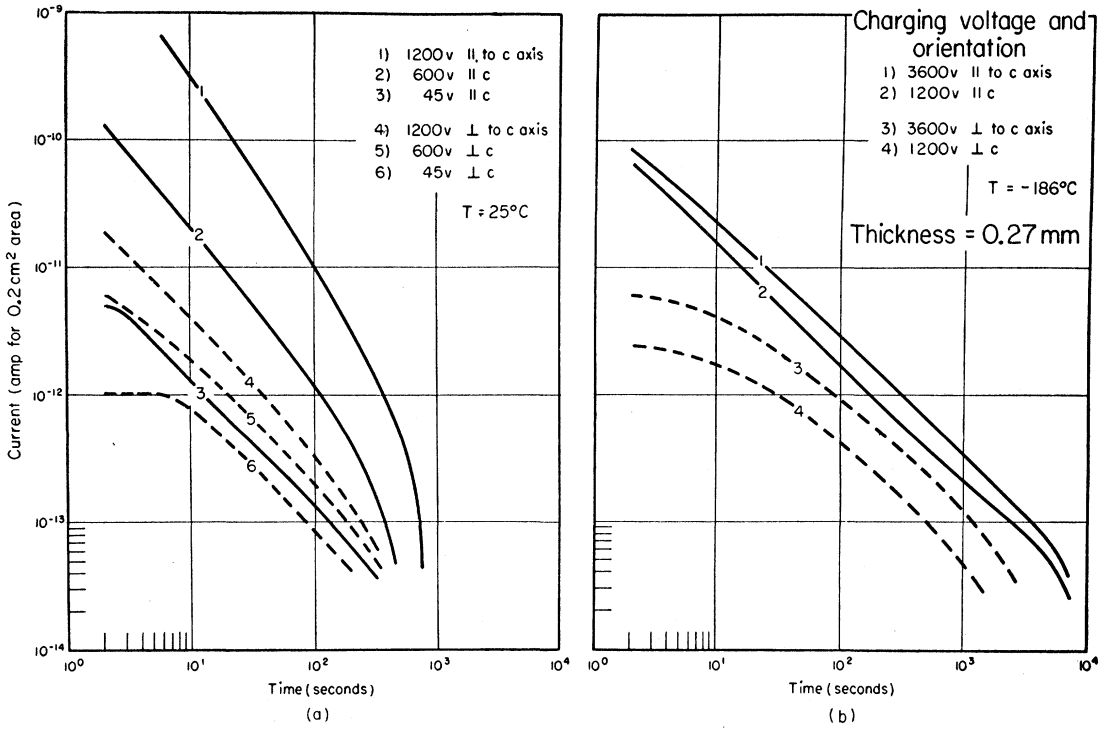

FIG. 6. Space-charge polarization as seen by short-circuit currents in rutile ∥ and ⊥ to axis at (a) room temperature, (b) −186°C.

trode. They have the typical pattern of positive Lichtenberg figures[5] (Fig. 8) and are drawn black into the crystal surface by reduction of the TiO_2.

The difference in final currents for various electrode materials at room temperature proved only noticeable at lower voltages and not startling. The exception was Ti, which produced currents increased by about one order of magnitude (Fig. 9). A comparison between gold and titanium electrodes in various combinations (Table I) shows that the influence arises only when Ti is the cathode, in keeping with the field-emission concept.

That light absorption in the tail of the "eigen-absorption" produces a photocurrent, and that this

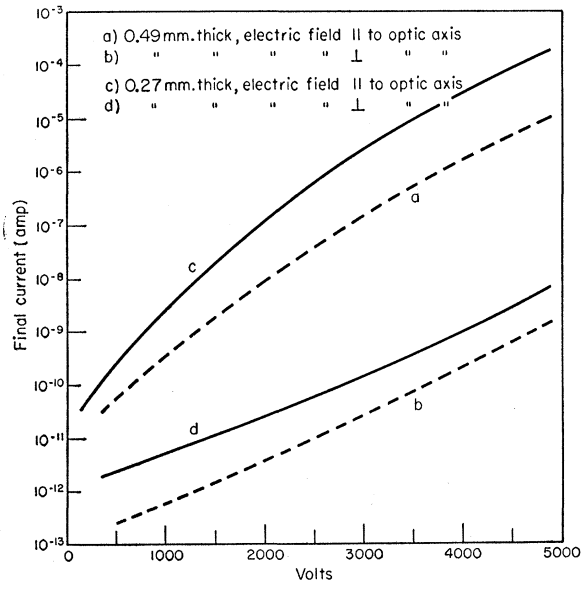

FIG. 7. Final currents at −186°C for crystals of 0.27- and 0.49-mm thicknesses.

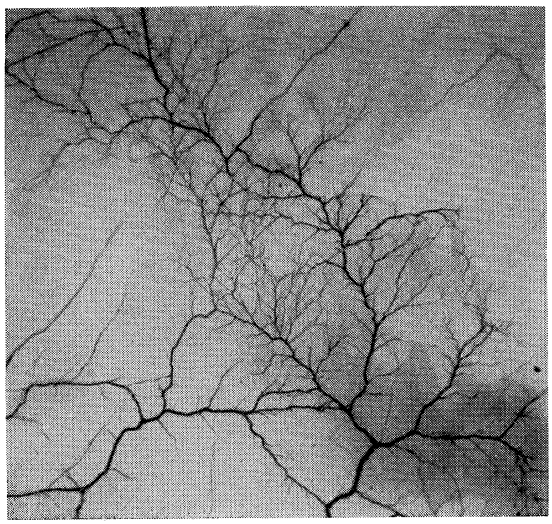

FIG. 8. Surface-discharge pattern at 240 kv/cm.

[5] F. H. Merrill and A. von Hippel, J. Appl. Phys. **10**, 873 (1939).

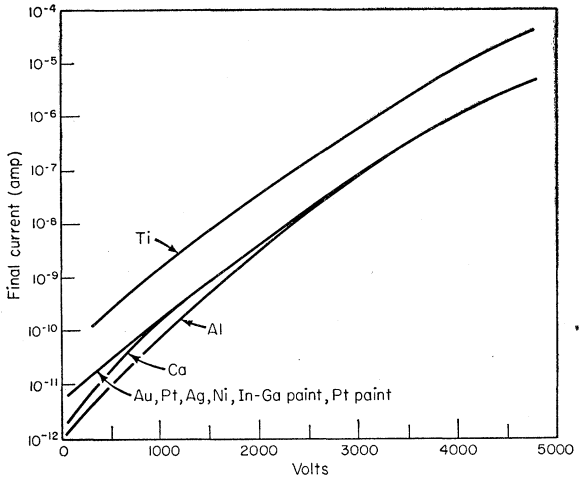

FIG. 9. Final currents for rutile || to axis at room temperature for different electrode materials (thickness 0.25 mm).

response and the optical absorption shift to longer wavelengths as temperature increases, has been studied in some detail by Cronemeyer.[3]

Measurements as function of light intensity with applied voltage as parameter show interesting complications introduced by field emission (Fig. 10). At 2 volts the photocurrent increases about proportionally to light intensity, as expected for normal photoconductors. At 6 and 8 volts, the dark current is still undetectable but the light current shows a rapid rise near the full intensity level. This sudden increase becomes still more pronounced at 10 volts (dark current 7×10^{-14} amp), where a change from half to full intensity increases the photocurrent about sevenfold. With

TABLE I. Influence of gold and titanium electrodes on the final current (room temperature) in various combinations.

Anode / Cathode		Ti / Ti	Ti / Au	Au / Ti	Au / Au
Final currents at 300 volts	||	8.2×10^{-9}	8×10^{-10}	8.2×10^{-9}	7.1×10^{-10}
	⊥	1.3×10^{-10}	2×10^{-11}	1.3×10^{-10}	1.7×10^{-11}

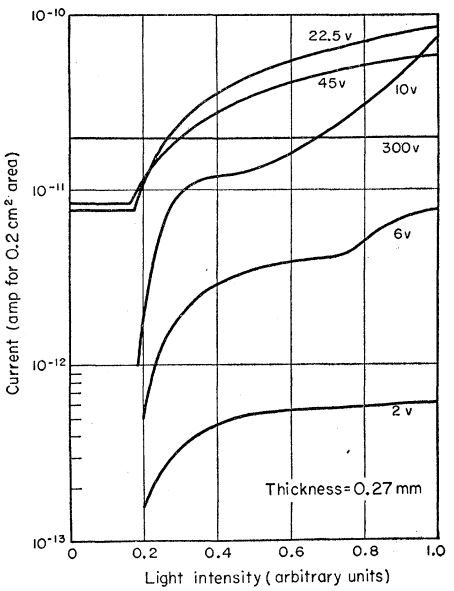

FIG. 10. Dc currents in rutile at 25°C ⊥ to axis as affected by illumination (wavelength 4210±5 A).

higher voltage the dark-current level moves up and the light influence begins to diminish, until at about 300 volts no photoeffect can be discerned with our present equipment.

As the preceding dark-current measurements suggest, the large nonlinear photosensitivity seems connected with the onset of field emission. In the critical transition region, light absorption may raise the current and thus change the field distribution sufficiently to push the crystal reversibly into the field-emitting state.

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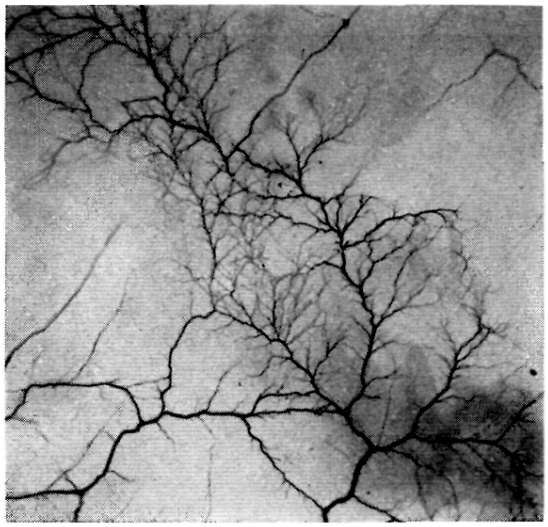

FIG. 8. Surface-discharge pattern at 240 kv/cm.