

## Optical Transmission and Photoconductive and Photovoltaic Effects in Activated and Unactivated Single Crystals of ZnS

GEORGE CHEROFF AND SEYMOUR P. KELLER

*Research Laboratory, International Business Machines Corporation, Poughkeepsie, New York*

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Certain physical properties of single crystals of ZnS and of ZnS activated with Mn, Cu, and Al have been determined. The optical studies involve transmission spectra. Photovoltages much larger than the energy gap have been measured. Reversals in the sign of the voltage have been measured as a function of the wavelength of incident light. The photovoltages and photocurrents have been determined as functions of wavelength and of intensity of incident light. A description is presented in which the characteristics of the crystals are treated as simple circuit elements.

### INTRODUCTION

ZINC-sulfide activated with Cu, Al, and Mn has been known to be dc electroluminescent,<sup>1</sup> i.e., the application of a dc electric field results in a constant light output which is characteristic of the  $Mn^{+2}$  ion present in the lattice. In the course of our studying the electroluminescent properties we observed photovoltages of an order larger than the energy gap with both activated and pure single crystals of ZnS. Such large voltages have been independently discovered elsewhere.<sup>2</sup> One can readily understand the existence of photovoltages smaller than the energy gap of the material in terms of typical semiconductor language, i.e., junction, rectifying contacts, concentration gradients, etc. However, photovoltages of an order larger than the energy gap cannot be so easily explained. A further complicating factor is the observation of reversals of the sign of the photovoltages with wavelength of incident light. These reversals make it less obvious that one can use the customary explanation to explain these effects. In order to arrive at an understanding of the basic phenomena involved we have measured electrical and optical properties of the materials. The course of this investigation is still in progress and measurements in addition to those presented in this paper will be needed before a fundamental understanding can be attained. We offer no explanation for the phenomena reported; however, we will present a description of the characteristics of the crystal treated as simple circuit elements.

### 1. EXPERIMENTAL PROCEDURES

#### A. Chemical Preparations

The phosphor powder was prepared by mixing commercial ZnS of "Luminescent" purity with 0.1%  $CuSO_4$ , 0.08%  $Al_2(SO_4)_3 \cdot 18H_2O$ , and 4.0%  $MnCO_3$ . The mixture was fired at 1200°C for one hour in an atmosphere of  $H_2S$ . It was then washed with KCN solution. The resultant powder (which was dc electroluminescent) was then placed in a sealed quartz tube containing 100

<sup>1</sup> Zalm, Diemer, and Klasens, Philips Research Repts. **9**, 81 (1954).

<sup>2</sup> L. Pensak, Phys. Rev. **109**, 601 (1958); B. Goldstein, Phys. Rev. **109**, 601 (1958).

mm pressure of  $H_2S$ . The tube was placed in a furnace that had a temperature gradient. The powder was in the hottest region which was maintained at 1200°C. The growing time extended for periods of 50–100 hours to assure reasonable uniformity and size of the crystals which grew from the vapor phase at a cooler region in the tube. The resultant crystals were spectrographically analyzed and the concentrations of the activators were in order of magnitude agreement with those added initially in the preparation of the phosphor powder. The crystals were in the shape of cylinders with hexagonal cross section, with lengths between 2 and 10 mm and thicknesses in the range of 1 mm. X-ray examinations performed by H. Dunn of this laboratory showed that they were of hexagonal structure. The single crystals of the base material were grown in the same fashion. The starting material was at first the same ZnS that was used in the phosphor preparation. This material proved to have a high Cu contamination. We then prepared ZnS which spectrographically showed no Cu impurities (thus setting the upper limit of the Cu concentrations to be 1 part in  $10^7$ ). This preparation was effected by heating Zn (99.999+ % purity) contained in a boat made of spectrographic graphite in a stream of  $H_2S$  bubbled through a  $Ba(OH)_2$  solution. The resultant crystals were colorless to the eye and showed only extremely slight fluorescence<sup>3</sup> under the action of uv light. It had been determined that concentrations of Cu of the order of 1 part in  $10^5$ – $10^6$  were effective at slightly darkening the crystals and making their fluorescence bright. The slight fluorescence we observed was perhaps due to excess Zn in the crystal, as reported frequently by other workers. As a result we are convinced that our crystals are of rather high purity.

#### B. Instrumentation

##### i. Optical Measurements

The apparatus is described in detail elsewhere.<sup>4</sup> The sample was mounted in front of the phototube which in turn was placed at the exit window of the Perkin Elmer

<sup>3</sup> The fluorescence was just barely detectable to a dark-adjusted eye.

<sup>4</sup> Keller, Mapes, and Cheroff, Phys. Rev. **108**, 663 (1957).

Model 112U spectrophotometer. In this way the chopped monochromatic radiation being transmitted through the crystal was measured. The fluorescent emission was separated from the transmitted light by means of optical filters.

### ii. Photoconductive Studies

The apparatus contained a Beckman Model DU monochromator having a high-pressure Xe arc lamp source. The crystals were electroded with an In-Hg amalgam which readily wetted them. They were mounted in air between supports held in a Teflon form. All the insulation was of Teflon. The photocurrents were measured with a Beckman vibrating-reed micromicroammeter and a General Radio electrometer.

### iii. Photovoltaic Studies

The light was supplied by the Beckman monochromator. The crystals were electroded and mounted as described above. The photovoltages were measured by two methods: (1) the open circuit voltage was measured using a General Radio electrometer which had an input impedance greater than  $10^{14}$  ohms, and (2) the photovoltage was balanced to zero using an electrometer as a null indicator. There was good agreement between both measurements.

## 2. EXPERIMENTAL RESULTS

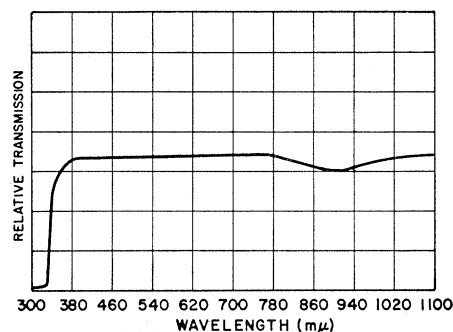
### A. Optical Measurements

The transmission spectrum for the activated samples is shown in Fig. 1(a). The curve is representative of many different samples as is that in Fig. 1(b), which presents the transmission spectrum of the unactivated ZnS. The essential difference between the two sets of data lies in the added absorption at 800–900  $m\mu$  in the case of the activated crystals. This absorption presumably is due to the presence of one of the activators. It probably is not Mn. In some phosphors the Mn does not absorb energy even though it does emit energy. This sensitized emission is believed to take place by means of energy transfer.<sup>5</sup> We accordingly assume that the Mn is not the center that is responsible for the visible absorption shown in Fig. 1(b). This long-wavelength absorption is undoubtedly related to a peak observed in the conductivity of the activated crystals in the same region. This will be discussed in the following sections. The apparent nonzero transmission shown below 330  $m\mu$  is believed due to edge emission. Further measurements are in progress concerning this.

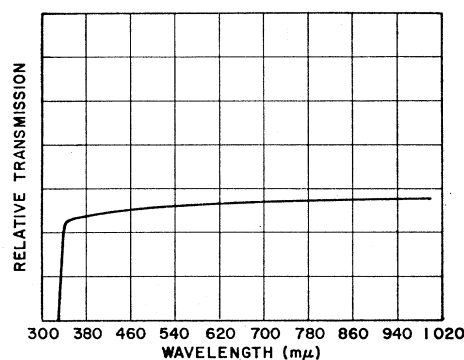
The results for the pure crystals are consistent with those reported elsewhere.<sup>6</sup>

<sup>5</sup> Th. P. J. Botden, Philips Research Repts. **7**, 197 (1952); Th. P. J. Botden and F. A. Kröger, Physica **14**, 553 (1948); R. J. Ginther, J. Electrochem. Soc. **101**, 248 (1954); D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

<sup>6</sup> W. W. Piper, Phys. Rev. **92**, 23 (1953).



(a)



(b)

FIG. 1. (a) Transmission spectrum of activated ZnS. (b) Transmission spectrum of unactivated ZnS.

### B. Photoconductive and Photovoltaic Studies

In the past, photocurrents have been measured by applying external voltages and thence measuring the response of the crystal to light. With materials that exhibit a large photovoltage, this voltage can be used in the same manner as an external voltage in measuring the photocurrents. One is not only interested in measuring the various dependences of the photocurrents, but it is also of interest to measure independently the photovoltage variables.

We have found that we can express all of these characteristics in terms of an extremely simple analog circuit which leads to consistencies of all of the data in terms of our measurements. This circuit is shown in Fig. 2. The photovoltage, or open-circuit voltage,  $V_0$ , is defined as that voltage measured across  $R_s$  when  $R_s \gg R_0$ , or alternatively as the negative of that voltage,  $V_e$ , necessary for no current to flow in the circuit. We define  $R_0$  as the resistance of the crystal. It will prove more convenient to deal with the conductance  $G_0 = 1/R_0$ .

It can be seen that

$$V_0 = i_s(R_0 + R_s), \quad (1)$$

where  $i_s$  is the current measured with no external voltage applied and a measuring shunt inserted in the circuit. For a given wavelength and light intensity  $V_0$  and  $R_0$  are constants. Hence the circuit is valid if

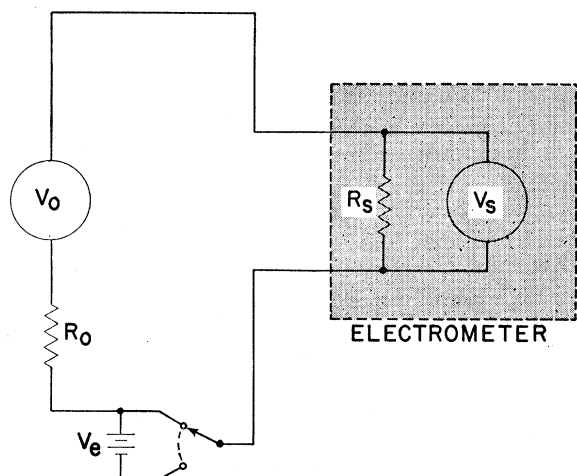


FIG. 2. Representative circuit of photoconductive and photovoltaic effects.  $V_0$ —open-circuit photovoltage;  $R_0$ —internal resistance of crystal;  $R_s$ —electrometer shunt;  $V_s$ —voltage measured across  $R_s$ ;  $V_e$ —external or balancing voltage.

$R_s/V_s$  is a linear function of  $R_s$ . This linearity holds for a large number of crystals for different wavelengths and different light intensities, and thus the representation is valid. A measurement of  $V_0$  by balancing it with  $V_e$  and a measurement of  $V_s$  for some  $R_s < R_0$  lead to a determination of the conductance,  $G_0$ .

We define  $i_0$  as the short-circuit photovoltaic current, or that current resulting when  $R_s = 0$ . It follows then that

$$i_0 = G_0 V_0. \quad (2)$$

If an external voltage ( $V_e$ ) is introduced into the circuit and if the representation still holds, then Eq. (1) can be written as

$$V_0 + V_e = i_e'(R_0 + R_s). \quad (3)$$

For  $V_e \gg V_0$  and  $R_s \ll R_0$ , we define the photocurrent  $i_e$  by

$$i_e = G_e V_e, \quad (4)$$

where  $G_e$  is the photoconductance. If  $G_0 = G_e$ ,  $i_e \propto G_0$  as the wavelength is varied and  $V_e$  is kept fixed. We found that  $G_0$  closely approximates  $G_e$ . This is not obvious since external voltages can seriously affect depletion layers and electrode barriers and thus numbers of current carriers.

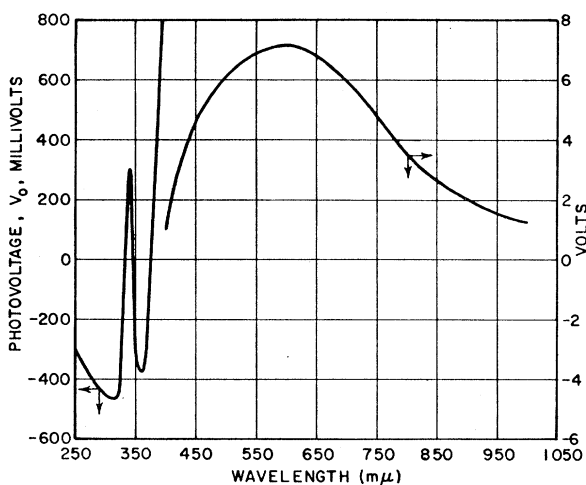
With this circuit and these definitions we have separated phenomenologically the two functionally independent variables,  $V_0$  and  $G_0$ . The data presented in the remainder of the paper indicate the validity of the model and the independent nature of  $V_0$  and  $G_0$ .

#### *i. Photovoltage, $V_0$ , versus Wavelength*

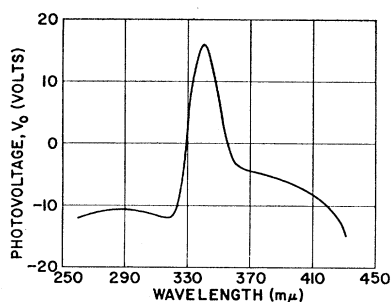
In line with our definitions above,  $V_0$  was measured in the two fashions and the results were always in agreement. It was found that the sign of the voltage varied with wavelength of incident light and what was

measured depended on the direction of the crystal in the circuit. We have chosen as positive that voltage which appears in both activated and unactivated crystals and is peaked at  $340 \text{ m}\mu$ .

Figure 3(a) depicts a typical determination of an activated crystal.<sup>7</sup> Some crystals had voltages as high as 20 volts in the visible region. In others the negative peak at  $360 \text{ m}\mu$  was present as a minimum in the positive region of the voltage. In a few crystals there was no negative voltage measured. Figure 3(b) contains a plot for a typical unactivated crystal. In the case of unactivated crystals the voltage measured varied from smaller voltages than those shown in Fig. 3(b) to larger ones (approximately 25 volts). We were unable to measure the photovoltage further into the visible region for unactivated crystals because of the very low conductivity. However, the measurements as far as they went into the visible region show no indication of a positive voltage in the visible region. The obvious



(a)



(b)

FIG. 3. Photovoltage  $V_0$  as a function of wavelength of incident light. (a) Activated crystal; (b) unactivated crystal.

<sup>7</sup> In this curve, as in the subsequent ones, normalization to constant energy or constant number of photons does not change the structure and the essential features of the curve. In fact, we shall show that  $V_0$  turns out to be independent of the intensity of the light over a large range of intensities, for various wavelengths.

difference between the two sets of data is the existence of a large measurable positive photovoltage band peaked at  $600\text{ m}\mu$  for the activated samples.

### ii. $V_0$ versus Light Intensity

The photovoltage was measured as a function of light intensity. Figure 4 presents typical data determined for activated crystals, which are similar to data obtained for different wavelengths on all the crystals, activated and unactivated. In most of the crystals measured we found a large range of intensity in which the photovoltage was constant. This was true for almost all wavelengths independent of whether  $V_0$  was positive or negative. However, near those wavelengths where  $V_0$  is changing sign this constancy was not maintained. In fact, one could get a reversal in voltage with intensity in these regions. Certain activated crystals showed a slight increase of voltage with increasing intensity while a small number showed first an increase and then a decrease as the intensity was increased.

### iii. Conductance, $G_0$ , versus Wavelength

Upon making use of the previous definitions,  $G_0$  was determined as a function of the wavelength of incident

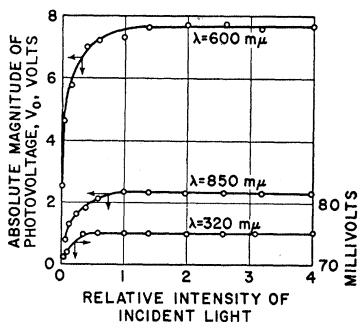


FIG. 4. Dependence of  $V_0$  on intensity of incident light for various wavelengths in the case of activated ZnS.

light. Figure 5(a) presents the results for the activated sample and 5(b) for the unactivated. The results were consistent for a large number of samples. The conductance peaked at  $800\text{ m}\mu$  for the activated samples is probably due to the same phenomenon that gave rise to an optical absorption at about the same region as shown in Fig. 1(a). The typical ratio of the conductance at  $800\text{ m}\mu$  to that at  $320\text{ m}\mu$  was 1/100. The ratio of the optical absorption at  $800\text{ m}\mu$  to that at  $320\text{ m}\mu$  was approximately the same. The very small peak at  $400\text{ m}\mu$  for the unactivated sample was found in every sample but to varying degrees. This may be due to some uncontrolled contamination (i.e., Cu, excess Zn).

### iv. $G_0$ versus Light Intensity

For both activated and unactivated crystals  $G_0$  proved to be proportional to the intensity of incident light, for all wavelengths. Figure 6 presents the results for the activated material. In the case of unactivated

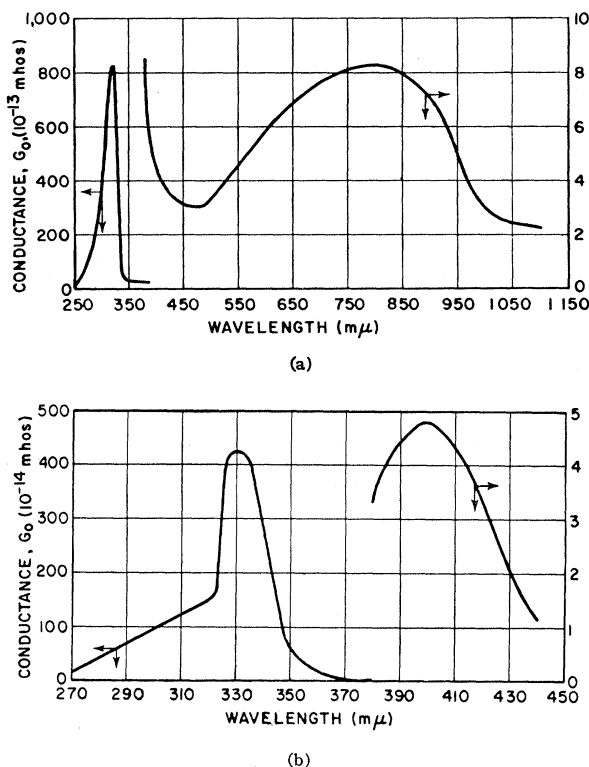


FIG. 5. Conductance  $G_0$  as a function of wavelength of incident light. (a) Activated crystal; (b) unactivated crystal.

samples, there was, of course, no measurable conductance in the  $600\text{--}800\text{ m}\mu$  region. Wavelengths in either the positive or negative photovoltage regions give straight lines for the conductance *vs* intensity curves. This linearity of  $G_0$  with intensity can be compared with measurements others have made on the dependence of photocurrents on light intensity.<sup>8</sup> Without making appreciable assumptions as to distributions and depth of traps, magnitude of the intensity of light, etc., we cannot remark on this observed intensity dependence.

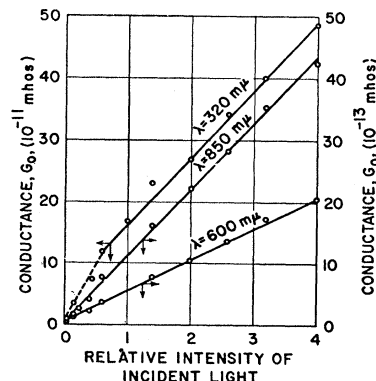
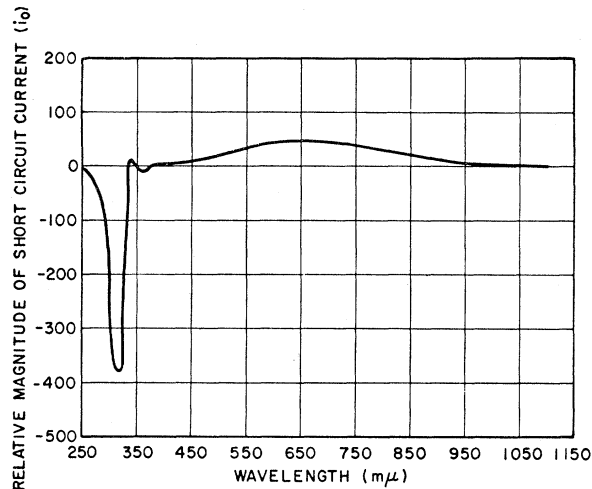
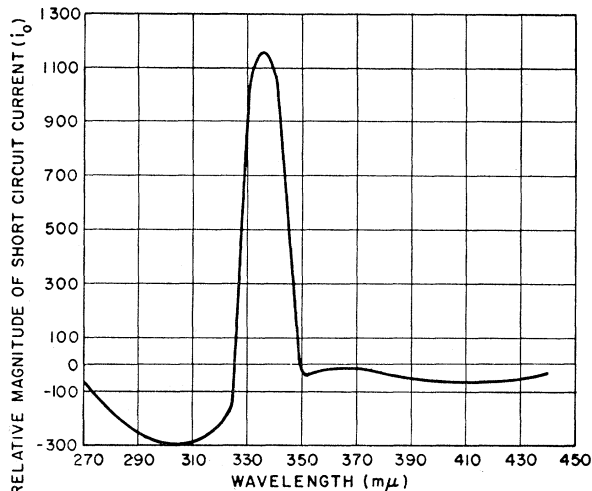


FIG. 6. Dependence of  $G_0$  on intensity of incident light for various wavelengths in the case of activated ZnS.

<sup>8</sup> G. F. J. Garlick, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19, p. 316.



(a)



(b)

FIG. 7. Calculated short-circuit photovoltaic current  $i_0$  as a function of wavelength. (a) Activated crystal; (b) unactivated crystal.

*v. Short-Circuit Photovoltaic Current,  $i_0$ , versus Wavelength*

We can calculate and plot  $i_0$  vs  $\lambda$  since both  $G_0$  and  $V_0$  have already been determined. Such a calculated plot can be then be compared to a measurement of  $i_0$  to check further the simple circuit presented in Fig. 2. A measurement of  $i_0$  can be effected if  $R_s$  is much less than  $R_0$  as is the case with a Beckman micromicroammeter. It turns out that the calculated  $i_0$  compares well to the

measured  $i_0$ . In some crystals the calculated and measured negative peak at 360  $m\mu$  of Fig. 7(a) is merely a positive minimum between 360 and 400  $m\mu$ . A similar calculated plot for the unactivated crystal is depicted in Fig. 7(b).

*vi.  $i_e$  versus Wavelength*

If an external voltage, larger than  $V_0$ , is applied, then from the discussion following Eq. (4) one would expect  $i_e$  to have the same wavelength dependence as  $G_0$ . This was found to be so and the plots obtained with such a voltage were essentially those shown in Fig. 5(a) and Fig. 5(b).

### 3. CONCLUSION

One can talk about the  $G_0$  plots in terms of standard phosphor language, namely short-wavelength conductance being caused by excitation of carriers across the energy gap and long-wavelength conductance being caused by excitation to or from traps, or impurity centers. As we mentioned, we need other kinds of measurements in order to understand the large photovoltages measured and their reversals. The explanation of these effects may be within the broad language of semiconductors; however, one may have to consider such things as the symmetry of the crystal. For example, the crystal belongs to the  $C_3$  symmetry class in that it has no plane of symmetry perpendicular to the  $c$  axis. We have already considered this symmetry or lack of it, as it is reflected in the paramagnetic resonance absorption of the Mn ions in the crystal.<sup>9</sup> The  $c$  axis is a polar axis and various measurements of physical properties are different with respect to a reflection along this axis; the crystal should exhibit a pyroelectric effect, the rate of etching in one direction along the  $c$  axis is different from the rate along the opposite direction. This polarity of the  $c$  axis may well play a role in the photovoltages observed. We plan to make certain investigations along these lines.

We also plan to investigate possible inhomogeneities in the crystals. We have already undertaken a photovoltage probe measurement and have observed for activated crystals in the visible region a continuous dependence of voltage on length. In the uv region, probing indicated reversals in sign along the length of the crystal.

### ACKNOWLEDGMENT

We wish to thank G. D. Pettit for making the spectral determinations.

<sup>9</sup> Keller, Gelles, and Smith, Phys. Rev. **110**, 844 (1958).

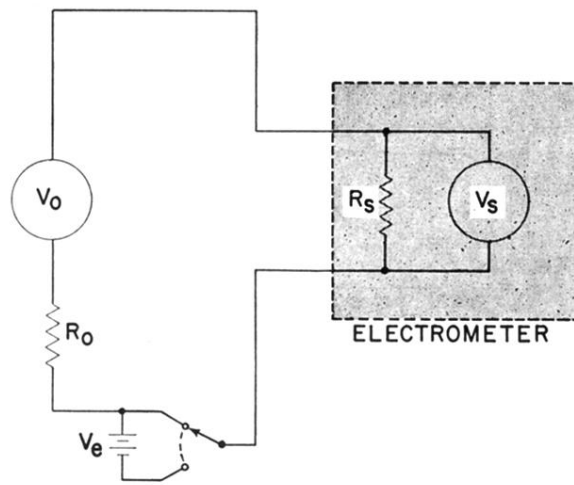


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