

## Electrical and Optical Properties of Indium Selenide

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The electrical and optical properties of InSe have been investigated with single crystals of the compound. The spectral dependence of the optical absorption coefficient and of the photoconductivity was measured. The optical absorption edge was not sufficiently well defined for the band gap to be estimated unambiguously. The photoconductive response was mostly in the visible, and its sensitivity comparable with that of gray selenium. The thermal activation energy of the electrical conductivity was about 1 ev in what is presumably the intrinsic region; and 0.2 to 0.4 ev, depending on the particular sample, at lower temperatures. Conflicting results for carrier type were obtained from several different experiments.

### INTRODUCTION

THE compound InSe was reported to be a "good" photoconductor by Kolomiyets and Ryvkin,<sup>1</sup> but, unfortunately, all their results were presented on relative scales and no mention was made of the electrical properties. Their measurements were all made either on ground and polished polycrystalline plates or on evaporated layers with various heat treatments in selenium vapor. Recently, measurements in this country on evaporated layers of InSe have been reported.<sup>2</sup> Single crystals of InSe were used for most of the work described in the present report.

### SAMPLE PREPARATION

The samples of InSe were prepared by reaction in vacuum of stoichiometric amounts of indium and selenium.<sup>3</sup> Most of the samples were prepared with 99.97+ percent indium from the Indium Corporation of America and with high-purity selenium from the American Selenium Company. One sample, designated "zone-refined" in later sections, was prepared with 99.999 percent selenium from Canadian Copper Refining and Smelting Company and with zone-melted indium. The compound prepared from these materials was also zone-melted in a dry hydrogen atmosphere.

The samples of InSe were crystallized in a small Stockbarger-type furnace. The ingots were approximately 1 cm in diameter and 2 cm long. The melting point of InSe is 660°C, and it was comparatively easy to grow large single-crystal regions in the samples. However, it was quite difficult to convert the entire sample into a single crystal. One early sample consisted of a number of needle-like crystals with a complicated monoclinic structure. Most of our samples, however, have had a mica-like structure, with one very easy cleavage plane. The structure of the mica-like material has not been determined, but a Laue photograph showed trigonal symmetry. A powder photograph had some lines in common with the pattern published by

Klemm and Vogel,<sup>4</sup> but was not identical. The crystal structure also appears to be different from that found recently for GaSe.<sup>5</sup>

Samples were cut with a jeweler's saw perpendicular to the cleavage plane, and by cleavage along the planes. The thin samples for optical measurements were prepared by successive cleavage of a sample pressed between two layers of Scotch tape. Contacts could be soldered to InSe with indium, but these contacts were not consistently ohmic. No completely satisfactory method of making contacts was found. Pressure contacts for high temperatures, and silver paste for room temperature and below, were fairly satisfactory and were used in most of the work.

### OPTICAL ABSORPTION

The optical absorption of indium selenide was measured on a series of layers cleaved from a single crystal, ranging in thickness from about 0.5 to 80 microns. The absorption coefficient calculated from optical transmission data is shown as a function of photon energy in Fig. 1. The optical thickness of the samples was determined from interference effects in the transmission region, and the refractive index from the reflection coefficient. The refractive index is about 3 in this region. The thickness measurements were verified with a micrometer on the thicker samples. The transmission was measured with a PbS detector and a 931-A photocell, with corrections for absorption of the sample support (Scotch tape), and for long-wavelength reflection. Only those data were used for which optical transmission was less than 10 percent, to eliminate interference effects. A rough check on these results was obtained by plotting transmission *vs* thickness at several wavelengths; this indicated that reflection effects were satisfactorily eliminated.

The absorption edge is not clearly defined, and there is the possibility that the absorption at low photon energy might be attributed to impurities. Data taken on "zone-refined" samples, however, showed no difference in the absorption constant at photon energies up

<sup>1</sup> B. T. Kolomiyets and S. M. Ryvkin, *Zhur. Tekh. Fiz.* **9**, 987 (1947).

<sup>2</sup> Donald E. Bode and Henry Levinstein, *J. Opt. Soc. Am.* **43**, 1209 (1953).

<sup>3</sup> W. D. Lawson, *J. Appl. Phys.* **23**, 495 (1952).

<sup>4</sup> W. Klemm and H. U. v. Vogel, *Z. anorg. u. allgem. Chem.* **219**, 45 (1934).

<sup>5</sup> K. Schubert and E. Doore, *Naturwiss.* **40**, 604 (1953).

to 2.2 eV, so we conclude that this absorption is a property of the InSe crystals grown from the melt; this does not exclude the possibility of a nonstoichiometric equilibrium under our conditions of preparation

### PHOTOCONDUCTIVITY

The photoconductive spectral response was also measured in cleaved layers, with the results shown in Fig. 2. These data were taken on samples of different thickness, and at different field strengths. The difference in spectral response at low energies is presumably caused by the different absorption. For the range of field strengths used, up to several thousand volts/cm, the photocurrent was proportional to the voltage in each sample. A similar spectral response was also observed for the photovoltaic effect, obtained by illuminating the sample asymmetrically.

We do not find the long-wavelength band of sensitivity observed by Bode and Levinstein,<sup>2</sup> but the main band of photoconductivity extends to longer wavelength in our cleaved layer than in their evaporated layers. We have also measured the photoconductive time constant, and find a value about one millisecond, essentially independent of wavelength from 0.6 to 1.2 microns. There was no evidence of the short time constant observed at long wavelength by Bode and Levinstein, which further indicates that the sensitivity in this region is probably due to imperfections in their films.

Kolomiets and Ryvkin<sup>1</sup> have measured optical absorption and photoconductive response in both ground plates and evaporated layers of InSe. We cannot compare our data, however, since they specified

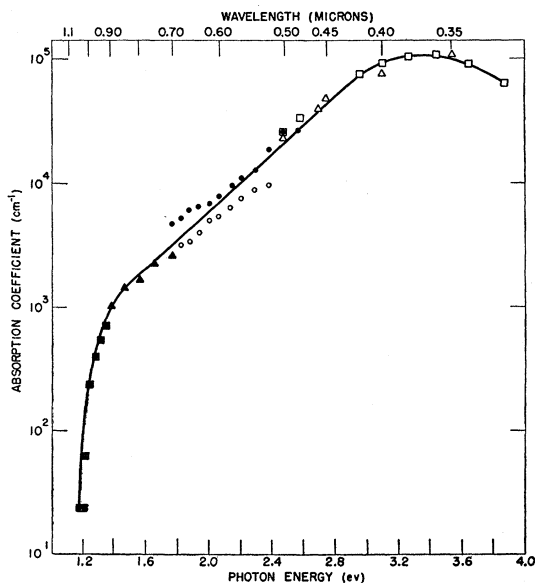


FIG. 1. Optical absorption coefficient of InSe. The different symbols refer to samples of various thickness, except that  $\blacktriangle$  and  $\circ$  refer to the same sample with different detectors.

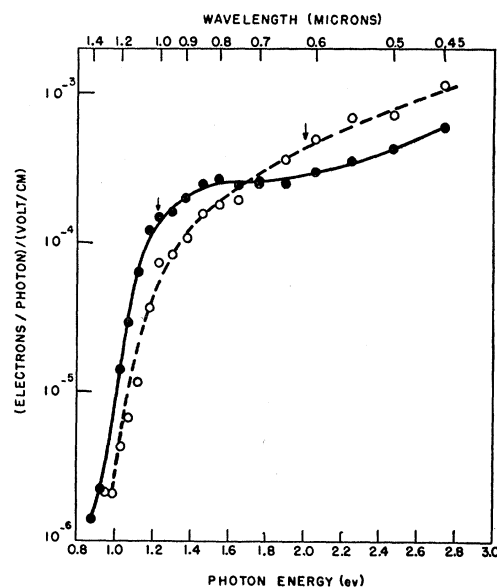


FIG. 2. Spectral dependence of the photoconductivity in InSe. The conductivity was measured parallel to the cleavage plane. The arrows indicate photon energy for 90 percent absorption in each sample.  $\circ$ —3 microns thick, 30 v/cm;  $\bullet$ —50 microns thick, 3000 v/cm.

neither the sample thickness nor the units in which incident light was measured.

### ELECTRICAL CONDUCTIVITY

The electrical conductivity of InSe was measured in a vacuum oven at pressures of about  $10^{-6}$  mm of Hg. The temperatures were measured with a platinum-platinum+10 percent rhodium thermocouple in metallic contact with the oven block. Some measurements were made using separate current and potential electrodes. However, these gave results identical with the simpler two-electrode system which was used for the results reported here.

Figure 3 shows the temperature dependence of the conductivity in several samples. The conductivity measurements were reproducible with increasing or decreasing temperature. The conductivity of the "zone-refined" sample was not measured as a function of temperature. The room temperature conductivity of this sample was  $5.3 \times 10^{-3}$  (ohm-cm)<sup>-1</sup> parallel to the cleavage plane, and  $8 \times 10^{-5}$  (ohm-cm)<sup>-1</sup> perpendicular to the cleavage plane. The line with slope 0.96 eV was common to all these samples in the higher temperature range. As the optical absorption data do not indicate an unambiguous "absorption edge," a comparison of this presumably "intrinsic" activation energy with the optical data does not seem fruitful.

### CARRIER TYPE

Several experiments were performed to determine the carrier type in single-crystal samples of InSe. An attempt to measure the Hall effect in two different

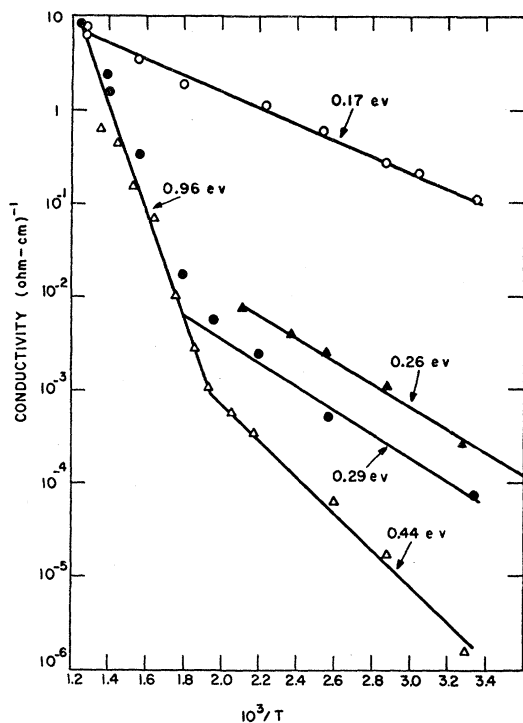


FIG. 3. Temperature dependence of the electrical conductivity of InSe. Activation energies are given for each sample.  $\circ$  polycrystalline;  $\blacktriangle$ ,  $\bullet$  single crystals, conductivity parallel to cleavage plane,  $\triangle$  single crystal, conductivity perpendicular to cleavage plane.

ingots was unsuccessful, although the sensitivity was sufficient to measure a mobility greater than  $0.1 \text{ cm}^2/\text{volt-sec}$  for a single-carrier type of semiconductor. With an etched tungsten point, rectification was observed corresponding to  $p$ -type conductivity. This was verified by the photovoltaic effect at the same point contact. However, thermoelectric power measurements, made without moving the tungsten point, indicated  $n$ -type conductivity. Further measurements of thermoelectric power on another sample from the same ingot showed  $p$ -type conductivity. These latter measurements were made with platinum-disk electrodes, and the thermoelectric power was essentially constant, at about  $200 \mu\text{volt}/^\circ\text{C}$ , from liquid nitrogen to room temperature. This uncertainty in the sign

of the thermoelectric power may be the result of a surface oxidation, since the last sample had been exposed to the air for several weeks, while the first had a freshly cleaved surface. The different sign of the carriers obtained from different experiments with the point contact can apparently be explained by assuming that InSe is not a single-carrier type of semiconductor, at least within the surface region.

These experiments were repeated on a sample cleaved from the "zone-refined" ingot. In this material, a Hall effect was measured corresponding to a mobility of  $5 \text{ cm}^2/\text{volt-sec}$ , with hole carriers. Measurements of the photovoltaic effect indicated  $n$ -type conductivity, however, as did the thermoelectric effect. The thermoelectric power in this sample was  $525 \mu\text{volt}/^\circ\text{C}$  at room temperature.

#### DISCUSSION

If one considers only the resistivity and Hall-effect data as being significant in indicating the properties of the bulk material, attributing the difficulties with rectification, photovoltaic, and thermoelectric effects to a surface layer, then from the mobility of  $5 \text{ cm}^2/\text{volt-sec}$  and resistivity of  $5.3 \times 10^{-3} (\text{ohm-cm})^{-1}$  for the "zone-refined" material, we can calculate a room-temperature carrier density of about  $6 \times 10^{15} \text{ cm}^{-3}$ . With no information on the mobility in the unzoned material, a carrier density cannot be calculated, but it appears from the resistivity change and from the optical absorption data that the principal effect of the zone refining has been to increase the carrier mobility. Since consistent results for carrier type, mobility, and carrier density cannot be obtained from our data on resistivity, Hall effect, and thermoelectric power, not much quantitative value can be attached to these interpretations.

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