JANUARY 1, 1941 PHYSICAL REVIEW VOLUME 59

Photoconductivity of a Natural Willemite Crystal*†

ROBERT C. HERMAN,** *Palmer Physical Laboratory, Princeton University, Princeton, New Jersey*

AND

ROBERT HOFSTADTER, *Randal Morgan Laboratory of Physics, University of Pennsylvania, Philadelphia, Pennsylvania*

(Received November 13, 1940)

This paper deals with the dependence of the photoconductivity of a natural single crystal of willemite on the wave-length of exciting light, temperature and time. The ultraviolet absorption spectrum of this crystal has been obtained.

INTRODUCTION

THE mineral willemite (zinc orthosilicate—Zn_2SiO_4) has played an important role in the development of luminescent materials. The behavior of zinc orthosilicate phosphors under electron bombardment as well as irradiation with ultraviolet light has been the subject of many investigations.[1] Until recently, the excitation spectrum for fluorescence of willemite was said to lie in the spectral range between 2200 and 3000A,[2] although it has been reported that excitation can be caused by irradiation with the neon resonance lines[3] as well as by Hg 3650A.[4] The work of Kroger,[1b] shows that the excitation spectra of zinc orthosilicate phosphors extend from about 2100A to beyond 5000A. Recently, Beese found willemite phosphors to fluoresce when irradiated with ultraviolet light in the spectral range from 3150 to 1400A.[5]

Some time ago, one of the authors (R. H.) found that both natural polycrystalline willemite and a willemite phosphor (1 percent Mn) prepared artificially exhibited photoconductivity in the spectral range from about 2500 to 3650A.[6] Since that time, the authors have studied the photoconductivity of a natural single crystal of willemite in the hope that some correlation might be found between it and the excitation spectrum. Recently, Hill and Aronin,[7] have reported photoconductivity in the case of pure and Mn activated zinc orthosilicate phosphors.

It is the purpose of the present paper to report results obtained on the dependence of photoconductivity on the wave-length of the exciting light, temperature and time as well as on the ultraviolet absorption of a natural single crystal of willemite.

EXPERIMENTAL

Figure 1 is a schematic diagram of the apparatus employed. Both the crystal and a calibrated thin window Na photo-cell (kindly lent to us by the General Electric Company) were mounted in vacuum. Electrical connections were made through leads sealed in Pyrex glass tubes. The photo-currents from the crystal (5×10^{-14} to 5×10^{-11} amp.) and the photo-cell (10^{-12} to 2×10^{-11} amp.) were amplified by separate FP-54 electrometer tube circuits so that it was possible to make simultaneous, independent measurements of photoconductivity and incident energy.[8] In this manner any fluctuations of the ultraviolet source (Hanovia Uviarc) were eliminated. The amplified currents from photo-cell and crystal were read by a Moll microgalvanometer (0.2-sec. period) and Moll galvanometer (1.5-sec. period), respectively. When absorption measurements

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* This work was done while the authors were at Princeton University.

† A preliminary account of this work was given at the Princeton Meeting of the American Physical Society, June 1939. See Phys. Rev. **56**, 212 (1939).

** Now at the Moore School of Electrical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

[1] For example, see (a) R. P. Johnson, Am. J. Phys. **8**, 143 (1940) and (b) F. A. Kroger, Physica **6**, 764 (1939).

[2] (a) J. W. Marden, N. C. Beese, and G. Meister, Trans. I. E. S. **34**, 55 (1939); (b) C. G. Found, Trans. I. E. S. **33**, 161 (1938), see p. 187.

[3] (a) A. Ruttenauer, Physik. Zeits. **37**, 810 (1936); (b) H. G. Jenkins and J. N. Botwell, Trans. Faraday Soc. **35**, 155 (1939); (c) M. Schon, reference 3(b), p. 162.

[4] A. Ruttenauer, Zeits. f. tech. Physik **19**, 148 (1938).

[5] N. C. Beese, J. Opt. Soc. Am. **29**, 278 (1939).

[6] R. Hofstadter, Phys. Rev. **54**, 864 (1938).

[7] A. G. Hill and L. R. Aronin, Phys. Rev. **57**, 1090 (1940).

[8] No corrections have been made for the loss of energy by reflection from the crystal in measuring both photoconductivity and absorption. In all but the absorption measurements the crystal was thick enough so that all the incident light not reflected was absorbed completely.

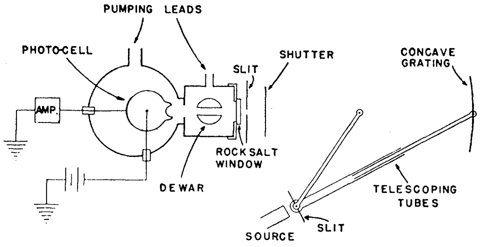

FIG. 1. Schematic diagram of apparatus.

were made a readjusted Zernicke type Ze galvanometer (1.3-sec. period) was employed. The ultraviolet source was mounted behind a slit which could be moved along the arc of a circle, in such a way that the source always pointed to the concave grating, by means of the arrangement shown in Fig. 1.[9] The optical system was such that the upper part of any mercury line fell on the crystal while the lower part fell on the photocell. Since the intensity along the height of the mercury lines varied in a different complicated manner for each line, it was necessary to make appropriate corrections. It was not realized at first that the intensity varied in this manner. This effect was probably caused by the fact that the concave grating was aluminized.[10] Related effects have been reported by Strong[11] who found that Wood anomalies[12] of spectral energy distribution were frequently developed by evaporating certain metallic films on gratings. So far as we know the particular effect we mention has not been reported in the literature. The necessary corrections mentioned above might have introduced an error of about ten percent only in the curves showing the dependence of photoconductivity on wave-length. All other curves shown in this paper do not depend upon this correction.

Figure 2 shows how the crystal was mounted in the Dewar vessel during part of these experiments. Temperature measurements were made with a calibrated copper-Eureka thermocouple mounted close to the crystal and connected to a Leeds and Northrup type K potentiometer. The voltage supplies for both the crystal and photocell were batteries contained in metal boxes, and were insulated from ground by means of Lucite supports standing on a layer of paraffin. All sensitive leads were insulated from ground by the use of Lucite plugs and were electrically shielded.

The single crystal of willemite, kindly given to us by the Geology Department of Princeton University, came from Franklin, New Jersey. It was uniformly pale green in color, transparent, uncracked and gave a green body fluorescence when irradiated with ultraviolet light or bombarded with electrons. The crystal was about 14 mm long and had four well-defined crystal faces whose dimensions were about 14×3 mm. Certain spectroscopic analyses on portions of the crystal have been made but the results are not entirely conclusive. However, it is certain that Mn, Mg and Fe are present. A microchemical analysis, kindly performed by Dr. E. H. Winslow, of the General Electric Company, gave the following data: Mn—0.70 percent, Fe—0.27 percent, Cu and Ni—less than 0.001 percent, if any.

Two parallel crystal faces, 2.0 mm apart, were polished and then sputtered with gold before mounting. The electric field was applied perpendicular to the long axis of the crystal and the direction of the light was perpendicular to both throughout these experiments. No attempt was made to study the effect of different crystal orientations. In order to make absorption measurements the crystal was ground and polished to a thickness of 0.3 mm. The absorption spectrum at room temperature was obtained in air by moving the crystal in and out of the light beam next to the exit slit of the ultraviolet monochro-

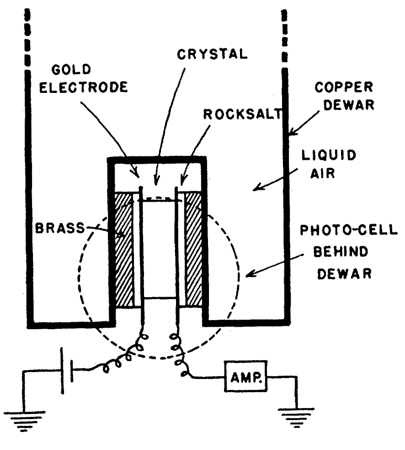

FIG. 2. Mounting of crystal in Dewar.

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[9] A similar arrangement was employed previously by one of the authors and Mr. F. B. Quinlan of the General Electric Company.

[10] This was kindly suggested to us by Professor Shenstone.

[11] J. Strong, Phys. Rev. **49**, 291 (1936).

[12] R. W. Wood, Phil. Mag. **4**, 396 (1902); **23**, 310 (1912).

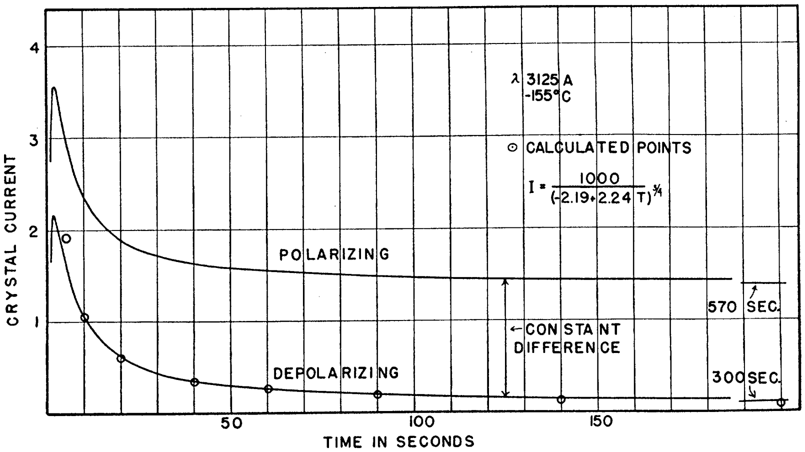

FIG. 3. Dependence of crystal current (in arbitrary units) on time.

mator. In obtaining the absorption spectrum at low temperatures (−145°C) the crystal was mounted on a fixed copper slit in contact with the Dewar vessel in order to avoid moving the specimen at low temperatures. By means of a shutter the energy transmitted through the crystal was measured as well as the energy in that part of the line that passed through the open slit below the crystal. This was repeated at room temperature. If the ratio of the two transmissions is taken, the result is a relative transmission spectrum. Since the room temperature transmission spectrum had been determined "absolutely," this relative transmission spectrum at low temperature could be converted into percentage transmission. Absorption spectra at room temperature were obtained photographically also.[13] Ultraviolet light from a hydrogen arc was focused on the crystal mounted in front of the slit of a Jobin and Yvon spectrograph. Eastman No. 33 plates were employed. The transmission of the crystal was obtained by comparing crystal transmission with intensity marks put on the plate by varying the exposure time. The plates were measured by means of a densitometer.

The procedures followed in making the other measurements reported in this paper will be discussed in the next section. All electrical measurements were made at different times with gold electrodes. These experiments were repeated in rough fashion with Aquadag electrodes and qualitative agreement was obtained in all cases.

RESULTS AND DISCUSSION

In order to find the dependence on time of the crystal current the procedure was the following: Initially the crystal was illuminated while its electrodes were grounded through the amplifier in order to put it in a "depolarized" state, that is to say, one in which the crystal is free from all charge. Red light approximately up to 1μ was not effective in releasing the charge, while ultraviolet light was highly efficient. The next step was to put the electric field on while the crystal was in the dark. The crystal was then illuminated with light of a given wave-length. On opening a shutter the crystal current was observed to rise very rapidly to a maximum and then drop off slowly to some equilibrium value. At intervals of one second (determined by a metronome) and less frequently as time went on, positions of the galvanometer spot were marked off and subsequently plotted. After equilibrium had been attained the electrodes were grounded through the amplifier with the crystal in the dark. If the crystal was again illuminated without delay (in our experiments this was done well within 30 seconds) a reverse current was caused to flow. This was measured in the manner already described. In all cases the current fell to zero immediately when the illumination was cut off.

It was found for various mercury lines that the current rises rapidly after illumination has begun and then decreases to a saturation value because a reverse field is set up in the crystal caused by polarization. The ratio of the maximum current to its saturation value was found to be about 2.5.

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[13] We wish to thank Dr. A. M. Chase of the Biology Department of Princeton University for allowing us to use his apparatus for these measurements.

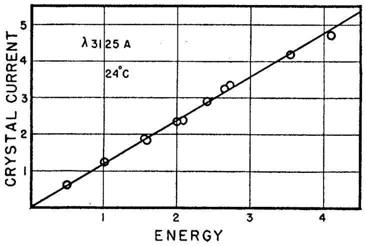

FIG. 4. Behavior of crystal current with respect to incident energy for constant voltage gradient.

These results are similar to those obtained for sulphur by Kurrelmeyer.[14] When the crystal is grounded through the amplifier and light is allowed to fall on it, a reverse current flows which has the same dependence on time as the photocurrent with the field on. Typical results are shown in Fig. 3. It is to be noted that the difference in the ordinates of these two curves is constant except at the beginning. These curves can be fitted best by the formula shown in the figure. Similar results have been obtained for different mercury lines and at different temperatures. If a set of such curves is taken for a given wave-length by varying the intensity of illumination, it is found that the difference between the ordinates is a constant for any pair of curves except during the first two or three seconds. Figure 4 shows how the crystal current varies as a function of intensity of illumination at constant voltage gradient. In this curve we have plotted the maximum crystal current, the crystal having been initially "depolarized." A straight line relationship is obtained also if one plots the saturation currents instead of the maximum currents. Figure 5 shows how the crystal current varies as a function of voltage gradient at constant intensity of illumination. The linearity of the curves shown in Figs. 4 and 5 furnishes evidence that we are dealing with primary currents. No signs of secondary currents were observed up to our maximum voltage gradient of 900 volts/cm for different wave-lengths and different temperatures. The dark current was found usually to be less than 10^{-13} amp. So far as we know the dark current did not vary (except for varying surface conditions). Therefore, we believe that no "excitation current" exists in willemite as it does in sulphur.[14]

We have obtained curves of photoconductivity per unit incident energy *versus* wave-length by measuring the maximum crystal current, the crystal having been freed initially of all charges, for each wave-length setting. However, similar curves using equilibrium currents gave the same spectral dependence except for a constant numerical factor. The results obtained are shown in Figs. 6 and 7 at the temperatures indicated and a constant voltage gradient of 900 volts/cm. Each curve shown has been obtained by averaging several runs. These curves have been drawn in each case so that the crystal current per unit incident energy at λ3022A is arbitrarily taken as unity. We should like to call attention to the fact that the crystal current per unit incident energy decreases as the temperature decreases and at different rates for different wave-lengths in such a way that the region of photoconductivity becomes narrower. For example at λ3022A the response decreases by a factor of about three in going from 93°C to −155°C, while at λ2537A this factor is about twenty-five.

Some structure is observed in all these curves, which we believe to be real. However, the corrections which had to be made might have exaggerated the structure.[15] In the room temperature curve of photoconductivity *versus* wave-length a peak appears near λ2753A. Hofstadter also has found such a peak while studying a natural polycrystalline sample of willemite obtained from Franklin, New Jersey, as well as with an artificially prepared phosphor activated with Mn.[6] Examination of Beese's fluorescent response curves for various types of willemite and a Mn activated phosphor shows a peak in this

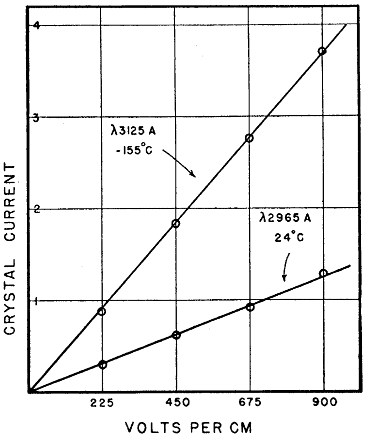

FIG. 5. Variation of crystal current (in arbitrary units) with voltage gradient at constant intensity of illlumination.

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[14] B. Kurrelmeyer, Phys. Rev. **30**, 893 (1928).

[15] See the experimental part of this paper.

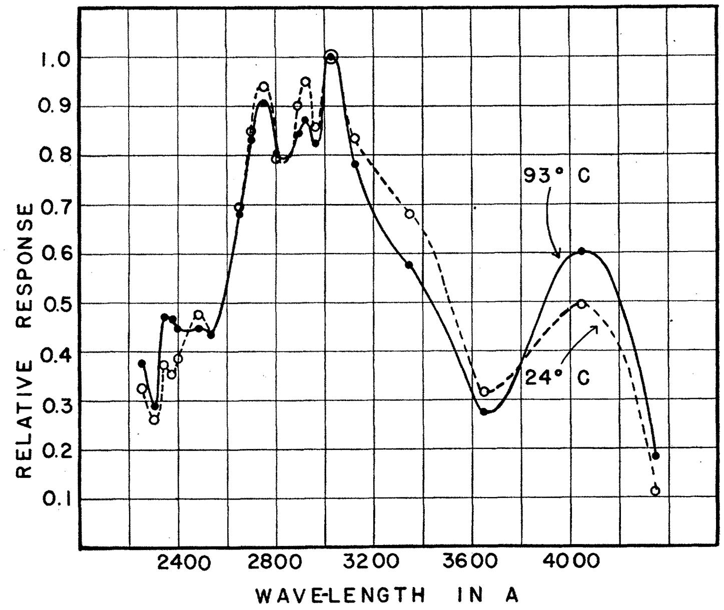

FIG. 6. Crystal current per unit incident energy (at constant voltage gradient) plotted against wave-length.

same neighborhood.[5] Both Beese and ourselves find a peak near λ2925A of which there was a slight indication in Hofstadter's curve *A*. Other coincidences seem to occur in the shorter wave-length region in Beese's and our own work, although Beese has not indicated that the structure in this part of the spectrum is real. We also find peaks of photoconductivity in the longer wave-length region which do not occur in Hofstadter's or in Beese's work. Their curves drop off sharply near 3000A. Perhaps the presence of different impurities accounts for this difference. However, Kroger's[1b] excitation spectra for Zn_2SiO_4-Mn phosphors also exhibit structure in the longer wave-length region. It is necessary to point out that there is no clearcut agreement between the data of Kroger and those of Beese and ourselves in this region.

It is well known that there is a close connection between photoconductivity and light absorption in a crystal. We wished to see whether there was some simple relation in the case of willemite. The absorption of the willemite crystal was obtained as described in the experimental section. Figure 8 shows the absorption spectrum obtained photographically and by direct transmission measurements made with a photo-cell. These absorption spectra agree qualitatively (the spectrum obtained by means of the photo-cell is more accurate) and differ from the absorption spectrum of pure Zn_2SiO_4 which has an absorption edge at about λ2200A as reported by Kroger.[1b] According to our results the absorption edge of our crystalline sample (0.70 percent Mn) lies in a very different position from the edge found for a willemite phosphor (1 percent Mn) by Kroger. We note that there is a side band on the long wave-length side of the absorption edge at about 3000A which is probably due to the 0.70 percent Mn or other impurities present in the natural willemite crystal. Kroger has also found such side bands in the absorption spectra of willemite phosphors activated with Mn. However, the absorption spectra we have obtained photographically do not exhibit the structure evident in his curves in the spectral range between 3500 and 4500A. The absorption spectrum of a natural willemite crystal discussed by Marden, Beese and Meister[2a] apparently does not show the band on the long wave-length side of the absorption edge.

An absorption spectrum was obtained also at low temperatures but is not given here because of its uncertainty. However, the low temperature spectrum is quite similar to that at room temperature except that both the absorption edge and the side band seem to shift to shorter wave-lengths. Until further studies are made on the effect of impurities on both photoconductivity

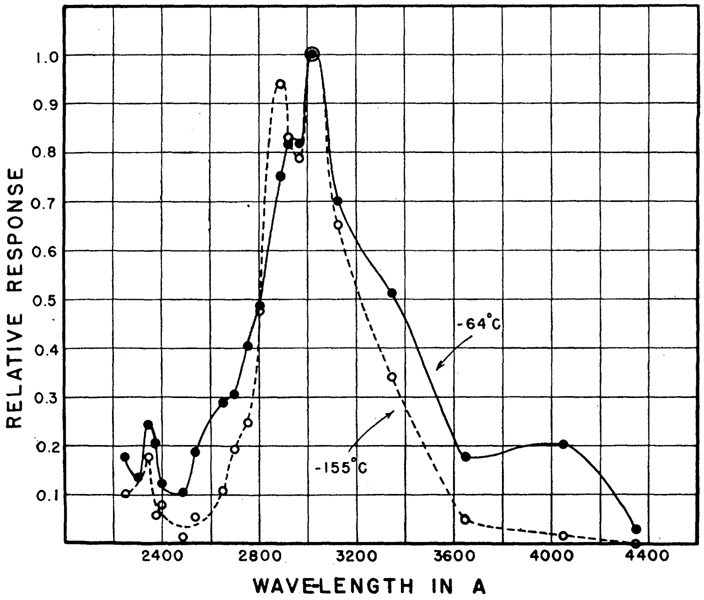

FIG 7. Photoconductivity at lower temperatures. See Fig. 6.

and absorption it is not possible for us to draw definite conclusions regarding relations between them.

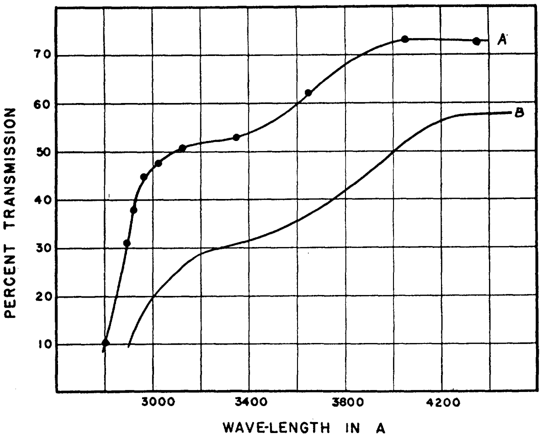

FIG. 8. Transmission of thin sample of crystal. Curve *A*—photo-cell. Curve *B*—photographic. Points on curve *B* were obtained generally at intervals of 10A. No interval was larger than 25A.

Some results on the dependence of the dark current on temperature have been reported previously.[16] At the present time we have nothing to add to the account already given.

ACKNOWLEDGMENT

We wish to thank the members of the Geology Department at Princeton University for their kind cooperation in many respects. We also wish to extend our appreciation to the General Electric Company for the interest they have taken in this work and for the aid they have given us. The Radio Corporation of America has kindly helped us in the analysis of our sample. It is a pleasure to thank Mr. W. Duryea and Mr. C. Grove for aid in building the apparatus and technical assistance. Finally, we appreciate the encouragement given us by Professor Shenstone.

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[16] R. C. Herman and R. Hofstadter, Phys. Rev. **57**, 936 (1940).