to evaluate $N(E)$ from absorption data in an unequivocal way. Thus, again, the discrepancy with the present work may not be serious.

Further experiments are planned to investigate in more detail the effects of lattice distortion and also to extend the measurements to solute elements of valency greater than two.

ACKNOWLEDGMENTS

Particular thanks are due to Mr. C. P. Mueller of the Technology Department of Westinghouse Research Laboratories for preparing the specimens used in this work. Thanks are also due to Dr. P. G. Klemens, Dr. C. B. Satterthwaite, and Dr. P. A. Flinn for their advice and interest in the experiments.

PHYSICAL REVIEW VOLUME 108, NUMBER 1 OCTOBER 1, 1957

Absorption of Light in Se near the Band Edge

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(Received June 19, 1957)

A photovoltaic method has been used to measure the relative absorption in hexagonal Se of photons of energy 1.6 ev to 2.0 ev in the temperature range 80°K to 440°K. The measurements show that the transitions are indirect at the band edge, requiring the absorption or emission of a phonon. The energy gap is found to be (1.79 ± 0.01) ev at 300°K; above this temperature $dE_G/dT=-9\times10^{-4}$ ev/degree. The absorption edge of hexagonal Se is compared with that of amorphous Se.

I. INTRODUCTION

A NUMBER of investigators has reported values for the energy gap in hexagonal Se. These values of E_G scatter considerably, ranging from 1.7 ev to 2.3 ev. Some of the earlier work has been summarized by Moss.[1]

The results referred to above were obtained from optical transmission measurements. Electrical measurements in Se have not been carried into the intrinsic region because of the low melting point (217°C) of Se.

Much of the scatter in the values of E_G may be attributed to certain experimental difficulties in making direct optical (transmission) measurements of the fundamental absorption, *viz.*: (1) The good Se single crystals available have been so small that very accurate measurements of transmission were not feasible. (2) The impracticability of preparing good hexagonal Se surfaces prevents an accurate direct measurement of reflectivity. (3) It is difficult experimentally to separate the absorption due to free carriers and imperfections from the fundamental absorption.

In this paper we present values for the fundamental absorption in Se as deduced from photovoltaic measurements.[2] Only the relative absorption coefficient is determined in our work. To get the absorption coefficient of Se from our data, an absolute measurement at one wavelength would be required.

The photovoltaic method for determining the absorption coefficient in Se has advantages over the transmission method since it avoids the large reflectivity correction. In addition, the results are simple to interpret in terms of the fundamental absorption, since free-carrier and impurity absorption do not contribute to the photovoltaic effect. We have found the photovoltaic method well suited for use with hexagonal Se.

The absorption near the band edge has been found to be of the form predicted for indirect transitions.[3] Accordingly, we have used a Macfarlane and Roberts plot[4,5] to determine values for E_G in Se. We have obtained in this way values of the energy gap accurate to 0.01 ev over a considerable temperature range.

An unusual feature of the results given here is that in fitting curves to our experimental points we find it necessary to use a phonon energy which varies with the temperature of measurement.

We have attempted to make similar measurements on amorphous Se cells in order to compare the absorption edges of amorphous and hexagonal Se. The results are somewhat ambiguous and we can interpret them only in part.

II. PREPARATION OF SAMPLES

Because Se is known only as p-type, a foreign n-type material must be used to complete the junction. However, we wish to measure only Se absorption. We first made measurements on commercial Se photovoltaic cells, but found a large spurious response which we believe is due to hole-electron pair production in

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[1] T. S. Moss, *Photoconductivity in the Elements* (Academic Press, Inc., New York, 1952), p. 192.

[2] W. J. Choyke and L. Patrick, Phys. Rev. **105**, 1721 (1957).

[3] Bardeen, Blatt, and Hall, in *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4–6, 1954* (John Wiley and Sons, Inc., New York, 1956), p. 146.

[4] C. G. Macfarlane and V. Roberts Phys. Rev. **97**, 1714 (1955).

[5] C. G. Macfarlane and V. Roberts Phys. Rev. **98**, 1865 (1955).

CdSe at the junction. Finally, following a suggestion of Dr. E. D. Wilson of this Laboratory, we were able to prepare samples which gave no spurious response.

A layer of Se on a metal plate (Ni-plated Al) was annealed for at least 2 hours at 200°C. Onto this was evaporated first a thin film of CdS and then a film of Au having about 30% white-light transmission. Contacts were made to the metal plate and the gold film. CdS forms the *n*-type part of the junction but does not have any photovoltaic response to photons of the energies used in this experiment.

To learn more about spurious responses and correction factors we made measurements on samples prepared in other ways. We mention three variations in preparation procedure.

(1) The annealing period was varied, giving us samples with varying amounts of amorphous or intergranular material. This enabled us to identify the response of the latter and also to learn the annealing treatment required to eliminate it.

(2) Annealing at 200°C *after* the evaporation of the CdS film introduced a response at lower energies (strongest at about 1.7 ev) which we believe is due to formation of CdSe at the Se−CdS interface. This response also appeared in samples prepared in the usual way when we attempted to make measurements above 170°C, thus limiting the range of good measurements.

(3) Substitution of Al for Au in the semitransparent film introduced a different correction curve for the metal-film transmission spectrum and enabled us to check the reliability of our correction.

III. EXPERIMENTAL PROCEDURES

The equipment was described in an earlier paper.[2] We shall describe here two correction curves which we applied to our data in getting the relative absorption constant β ($\beta = b\alpha$, where α is the absorption constant in cm^{-1} and b is a constant for a given temperature).

(1) Transmission measurements were made on glass slides exposed with the samples during evaporation of the CdS and the Au or Al semitransparent electrodes. Thus, we were able to correct for absorption and reflection by the Au or Al films. The correction factor varied slowly with wavelength, and the total variation was always less than 20%.

(2) A more important correction is that for nonlinearity of the sample response. Experimentally the problem is to measure the relative rate of hole-electron pair production as a function of wavelength λ by a certain incident flux N of photons per second. If the response is linear, as it usually is for low signal levels or high temperatures, then the signal (S) is proportional to $N\beta$ at all λ's and a measurement of the incident light spectrum enables us to plot β *vs* photon energy.

If the response is not linear we observe that, for a given sample and temperature, the departure from linearity is a function of S *only*. We then measure S *vs* N at constant λ and plot S *vs* S/N. The curve thus obtained is applied to our data to find from S a number proportional to $N\beta$ at any λ, thus permitting us to find β *vs* photon energy as before.

We have confidence in these corrections, since, although there was considerable sample to sample variation in the *uncorrected* data, the corrected curves were in good agreement.

IV. RESULTS

Hexagonal Se

In Fig. 1 we have plotted $\beta^{\frac{1}{2}}$ *vs* photon energy for sample $G3$ at three temperatures. β is proportional to the absorption constant α, which can be obtained from our data by using a good transmission measurement at a single wavelength to normalize our measurements. A sufficiently dependable value of α is not yet available, however.

The solid lines are calculated from the formula

$$\beta = 30\,000 \left[\frac{(h\nu - E_G + k\theta)^2}{e^{\theta/T} - 1} + \frac{(h\nu - E_G - k\theta)^2}{1 - e^{-\theta/T}}\right], \quad (1)$$

where $h\nu$ is the photon energy in ev, E_G is the energy gap, and $k\theta$ is the energy of the phonon absorbed or

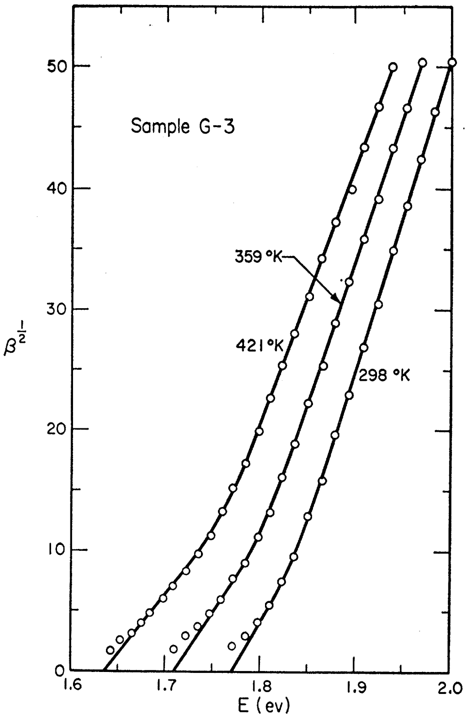

FIG. 1. The points are $\beta^{\frac{1}{2}}$ *vs* photon energy for sample $G3$ (hexagonal) at three temperatures. β is proportional to the absorption constant. The lines are calculated from Eq. (1) using the values of E_G and $k\theta$ chosen for best fit to the experimental points. These values are, respectively, 1.794 ev and 0.025 ev at 298°K; 1.743 ev and 0.035 ev at 359°K; 1.686 ev and 0.05 ev at 421°K.

emitted. This is the formula used by Macfarlane and Roberts[5] with their constant A set equal to 30 000. Our measurements do not, of course, determine the constant A. The value of 30 000 was estimated from transmission measurements[6] and is believed accurate to within a factor 3.

We present only three curves in Fig. 1, but we have made measurements at many temperatures in order to trace out the curves of Fig. 2, which show the temperature dependence of E_G and $k\theta$.

The results presented in Figs. 1 and 2 were obtained from a single sample. We have made extensive measurements on about 10 other samples, and after applying the corrections described earlier, we find good agreement with the results presented here. The values of E_G for best fit show a sample to sample variation of less than 0.01 ev above room temperatures and less than 0.02 ev at lower temperatures. The values of $k\theta$ are fitted within 0.005 ev above room temperature but are less certain at low temperatures. We could not fit the phonon absorption part of the 80°K curve at all; our value for E_G at 80°K assumes a phonon energy of 0.02 ev as obtained by extrapolation of the higher temperature values. An uncertainty in choice of $k\theta$ introduces an uncertainty of about the same amount in E_G.

Our properly prepared samples are free of the CdSe response. However, there is some response from amorphous or intergranular material even in the best annealed samples and it gives our curves a small low-energy tail. We have made a partial correction by subtracting a constant amount from β. This constant amount is about 10 at all temperatures and is thus less than $\frac{1}{2}$ of 1% of the higher data points in Fig. 1.

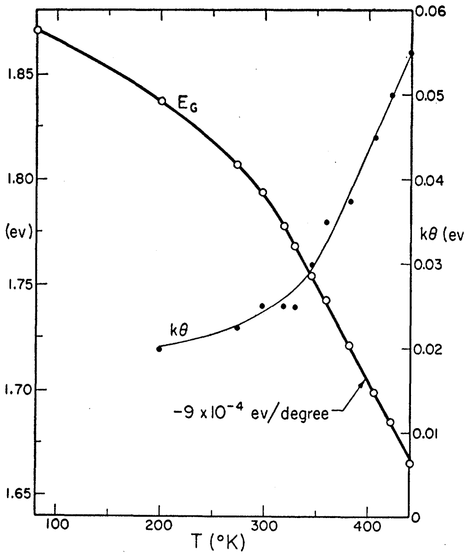

FIG. 2. Temperature dependence of E_G and $k\theta$ for hexagonal Se.

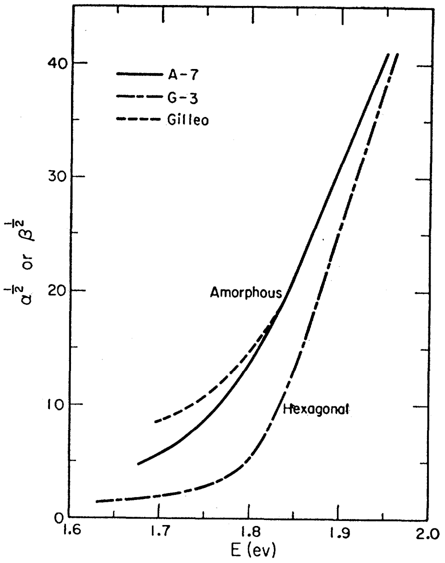

FIG. 3. Comparison of amorphous response (*A*7 and Gilleo's) with that of hexagonal Se (*G*3). Normalization of the *A*7 measurements brings them into coincidence with Gilleo's throughout the range $\alpha^{\frac{1}{2}}=20$ to $\alpha^{\frac{1}{2}}=40$. The $\alpha^{\frac{1}{2}}$ *vs* energy plot has no theoretical significance for *A*7 and is used merely for the comparison with *G*3. Measurements for sample *G*3 are given on the $\beta^{\frac{1}{2}}$ scale.

Consequently, it makes little difference in fitting the data—the only significant change is a reduction in the chosen value of θ of about 10%. The form of the amorphous response has been investigated at length and will be described in the next section.

Amorphous Se

We attempted to measure the photovoltaic response of cells made as described earlier except that amorphous (unannealed) Se was used instead of hexagonal Se. The response was insufficient to make meaningful measurements; perhaps a satisfactory *p*-*n* junction was not formed.

However, we were able to make good measurements on cells which had been annealed at low temperatures for short periods (sample *A*7 of Fig. 3 had been heated at 100°C for 1 hour). In such cells there is a mixture of hexagonal and amorphous Se. The photovoltaic response is quite different at the absorption edge from that of the well-annealed sample *G*3, but increasing the annealing progressively changes the response toward that of *G*3. After sufficient annealing to produce the *G*3 response, further annealing makes no change. We attribute the change in response to conversion of amorphous material to crystalline Se.

Transmission measurements indicate that the absorption coefficient of hexagonal Se is greater than that of amorphous at photon energies over 2 ev. We find the reverse to be true at 1.8 ev, hence the curves of absorption coefficients must cross. The crossing point is about 2 ev in Fig. 3 with our choice of 30 000 for the constant A.

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[6] J. J. Dowd, Proc. Phys. Soc. (London) **B64**, 783 (1951).

It is apparent that nearly all of the *A*7 response below 1.8 ev, and a considerable amount above, must be that of amorphous Se. We therefore compare the *A*7 measurements with transmission measurements by Gilleo[7] on amorphous Se films. The fact that his points lie above ours at low photon energies may be attributed to impurity absorption, which the photovoltaic method does not measure.

The energy dependence of the amorphous Se response in the range 1.7 ev to 1.8 ev is similar to that of the tail of sample *G*3; hence we think the latter is due to residual amorphous material. We found the temperature dependence of the amorphous response to be such that its contribution to the tail of *G*3 remained about the same at all temperatures.

V. DISCUSSION

We find a very sharp drop in absorption coefficient at the absorption edge, in contrast to previous results of Dowd[6] and Gilleo.[7] In this region the photovoltaic method gives a much more direct measurement of the fundamental absorption than the transmission method, as we pointed out earlier. We believe the greatest uncertainty in previous measurements was in the reflection correction. We therefore disagree with Moss,[8] who interprets Dowd's results as showing an unusually high absorption of 600 cm^{-1} by free carriers.

Previous measurements[7,9] have shown an increase in absorption at all wavelengths in a Se film converted from amorphous to hexagonal. This has been interpreted as showing a considerably larger energy gap in the amorphous form.[10] Our results show that in the tail, at least, the hexagonal form actually has a smaller fundamental absorption.

We know of no theoretical model that is satisfactory for making a quantitative interpretation of the amorphous absorption edge. Because the material is amorphous, one might expect that there is not a well-defined energy gap. The large tail is consistent with such a view.

The measurements by Gilleo[6] and Stuke[10] on hexagonal films show a strong absorption beginning at about 2.5 ev, which is beyond the range of our measurements. This may signify the onset of direct transitions.

Some calculations of the energy band structure of Se have been made[11] but they involve many approximations, and in their present form predict direct transitions at the band edge. The absorption edge derived from such a band structure would not be of the form we have found.

Because a phonon energy varying so strongly with the temperature is difficult to understand, we looked for alternative interpretations of our results. In particular we tried, unsuccessfully, to fit the curves by assuming that two phonon energies were involved. We are convinced that such a model cannot explain our results. Because the phonon energy determines both the relative slopes and the distance between intercepts on the energy axis of the two modes of absorption (with phonon emission or with phonon absorption) there is little freedom of choice in fitting the data. We therefore feel that the temperature-dependent phonon energy should be accepted. We may point out that, with increasing temperature, hexagonal Se expands in directions perpendicular to the *c* axis, but *contracts* along the *c* axis. This could give an unusual temperature dependence to the potential and hence to the energy band structure.

The value of *A* we have used in Eq. (1), (30 000), is about 10 times that found for Ge, Si, and SiC. We shall not attempt to calculate *A* from the formula given by Bardeen, Blatt, and Hall because the necessary parameters are not known well enough. However, if the hole-phonon interaction in the absorption process is the same as that which determines the mobility, *A* should be inversely proportional to the mobility, which is very small in Se ($\sim$1 cm^2/volt sec). Hence a large value of *A* is not surprising.

VI. SUMMARY

Using hexagonal Se photovoltaic cells, we have measured a relative absorption coefficient β, and we have normalized β in such a way that we believe it to have the same magnitude as α. Only the lack of reliable transmission measurements prevents us from presenting the absorption data in absolute units.

We find that the energy dependence of the absorption is that predicted for indirect transitions. From the relative absorption, β, we have evaluated the energy gap E_G and the energy, $k\theta$, of the phonon which is absorbed or emitted. We find it necessary to assume that the energy of the phonon in the indirect transition varies with the temperature of measurement.

With photovoltaic cells containing an appreciable fraction of amorphous Se we have found a tail at low energies which we attribute to amorphous Se. This absorption, after normalization, is in fair agreement with measurements of Gilleo on transmission of amorphous Se films.

We have found no way of interpreting the absorption of amorphous Se in terms of an energy gap. The relatively flat tail may indicate that there is not a well-defined energy gap.

ACKNOWLEDGMENTS

We wish to thank Dr. E. D. Wilson for much information about Se and Se photovoltaic cells.

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[7] M. A. Gilleo, J. Chem. Phys. **19**, 1291 (1951). Because good samples for transmission measurements can be prepared, the absorption coefficients reported for amorphous Se are reliable.

[8] T. S. Moss, reference 1, p. 198.

[9] J. Stuke, Z. Physik **134**, 194 (1953).

[10] T. S. Moss, reference 1, p. 203.

[11] J. R. Reitz, Phys. Rev. **105**, 1233 (1957).