section. Every part of the crystal starts to transform at the same time, in contrast to the slow transition with its one or two nucleation points. The transition process is also very different from the polarization reversal in the tetragonal phase. The latter always takes place through nucleation and growth of antiparallel domains. The reversal time varies continuously and exponentially with the electric field except that it must also be limited by the velocity of sound.[8] This is as expected since it must be more difficult to reverse an already established polarization than create or destroy one.

ACKNOWLEDGMENTS

The author is greatly indebted to Professor A. von Hippel for suggesting the problem and for his constant advice and encouragement throughout the course of this work. Various members of the Laboratory for Insulation Research contributed to the progress of this work by discussion of the many experimental and theoretical problems encountered.

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Optical Absorption and Photoconductivity in Magnesium Oxide Crystals*

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Optical absorption and photoconductivity spectra of magnesium oxide crystals from various sources are presented. The effects of ultraviolet and x-ray irradiation are described, and the results are interpreted in terms of valence changes of impurities, principally iron. A method for the analysis of the photoconductivity data is given. This method corrects for the effects of strong nonionizing absorption, which may lead to spurious peaks in photoconductivity spectra. The sign of the optically excited charge carriers was deduced by a method which involves the formation of a space-charge field by the motion of carriers in an applied electric field, and the detection of the asymmetry in this space-charge field when carriers are subsequently allowed to move under the influence of the space-charge field only.

A band centered at 5.05 ev has been detected in all specimens measured and this is believed to be due to the impurity Fe^{2+}. Irradiation in this band provides free electrons some of which are believed to be trapped by other Fe^{2+} ions. Three absorption bands previously observed by other authors are believed to be associated with the impurity Fe^{3+}.

1. INTRODUCTION

THE work to be described in this paper was part of a program[1,2] whose purpose was the determination of the nature of certain imperfections in magnesium oxide crystals. The imperfections of interest are those which evidence themselves as electronic excitation processes occurring in a region of the spectrum where light is not absorbed by the perfect crystal. According to the usual usage of the term, they may therefore be denoted as "color centers."

One of the principal reasons for the interest in color centers in MgO is the desirability of extending the information and understanding that has been gained in the study of the alkali halide group of compounds,[3] to a compound of divalent elements with a similar type of binding. So far as the author is aware, there is not in the present nor in any previous work, any evidence that an analog to any of the well-known color centers has been found in MgO. There are known, however, several optical transitions[4,5] which can be introduced in certain ways. The purpose of this work was to study these transitions by the measurement of absorption and photoconductivity spectra and to attempt to determine the nature of the corresponding imperfections.

Measurements of this sort have previously been published: optical absorption spectra by Weber[4] and photoconductivity spectra by Day.[5] Their conclusions have been extensively used by other authors in the discussion of measurements of conductivity,[6] ultraviolet activation,[7] luminescence,[8] and Hall effect[9] of MgO crystals.

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[1] Soshea, Dekker, and Sturtz, J. Phys. Chem. Solids **5**, 23 (1958).

[2] B. V. Haxby (to be published).

[3] F. Seitz, Revs. Modern Phys. **26**, 44 (1954).

[4] H. Weber, Z. Physik **130**, 392 (1951).

[5] H. R. Day, Phys. Rev. **91**, 822 (1953).

[6] E. Yamaka and K. Sawamoto, Phys. Rev. **95**, 848 (1954).

[7] F. P. Clarke, Phil. Mag. **2**, 607 (1957).

[8] E. Yamaka, Phys. Rev. **96**, 293 (1954).

[9] E. Yamaka and K. Sawamoto, Phys. Rev. **101**, 565 (1956).

TABLE I. Spectrographic analysis of a typical specimen.[a]

Element	Concentration (atomic %)
Fe	0.01–0.03
Mn	0.005
Cr	0.001

[a] See reference 2.

It is believed, that the measurements and interpretations of these two papers[4,5] err sufficiently in detail that one can be led to confusion concerning the energy level diagram necessary to make consistent all the data presently available. In the following we attempt to show the reasons for our disagreement with previous data and to construct a partial energy level diagram.

2. EXPERIMENTAL

2.1 Source and Purity of Material

Most of the crystals used in these experiments were obtained from the Norton Company, Niagara Falls, New York. A few were also obtained from the Infrared Development Company, Welwyn Garden City, Herts, England and others from the Advanced Lamp Development Laboratory of the General Electric Company, Cleveland, Ohio. Except where a particular reason exists, the sources of the individual specimens are not identified in the following sections. Haxby[2] has made extensive spectrographic analyses of material from all three sources and a typical result is reproduced in Table I. The material to which the table applies is referred to in the following as "normal," which designation is meant to imply that a large proportion of the samples measured had similar impurity concentrations.

2.2 Specimen Preparation

Crystals about 5×10 mm on the faces and from 0.2 to 1.0 mm thick were cleaved from larger pieces which had been selected for their lack of visible optical absorption. Some of the crystals were heated in vacuum before use. Such heat treatments were carried out in a small furnace operating inside a bell jar. The pressure was usually about 5×10^{-5} mm Hg. To prevent contamination of the crystal faces during the heat treatment, they were placed in a boat ground from a large MgO crystal, and a MgO slab lid was tied on with molybdenum wire.

Crystals were prepared for photoconductivity measurements by painting electrodes of air-drying silver paste (Dupont No. 4817) on two opposite edges. They were held between Teflon blocks, also coated on one face with the same paste, inside a light-tight box which could be desiccated when necessary.

2.3 Apparatus

A Bausch and Lomb grating monochromator was used to provide the illumination. The dispersion was 33 A/mm, and the monochromator was normally used with slits of 3 mm or less in width so that the band width was normally about 100 A or less. At 5 ev this corresponds to an energy range of 0.2 ev in the monochromator output, and the energy spread decreases as the square of the energy. Sharp-cut glass filters were used to remove the higher order dispersions.

The output of the monochromator passed through a fused quartz plate set obliquely to the beam so that a fraction of the beam was reflected to a Type 935 photocell, while the main beam was focused on the sample. The photocell was calibrated in a separate experiment by placing a calibrated thermopile in the sample position and measuring the output of both photocell and thermopile as a function of wavelength. The photocell could then be used to measure the light intensity corresponding to each measured photocurrent. Three light sources were employed to cover the energy range from 1.7 to about 5.6 ev. A carbon arc, using a National Carbon Company Type *W* cored anode, operating at 40 v, 60 amp, could be used over the entire range. More stable output was obtained from a General Electric Company Type *AH*6 high-pressure mercury arc (2.3–4.6 ev) or a tungsten lamp (1.7–2.3 ev). At energies greater than 5.0 ev there was an appreciable amount of stray light in the monochromator output. This was accounted for by measuring the decrease in photocurrent and light intensity when a Corning 9700 filter was placed in the beam. This filter cut off the energy at which the measurement was being made but passed practically all the stray radiation.

Owing to the lack of sensitivity, the photocell could not be used at quantum energies below 2.30 ev. By using the calibrated thermopile the variation of the output of the tungsten lamp with energy was determined in a separate experiment. Then, under a given set of conditions, the intensity could be measured at 2.3 ev using the photocell and the intensity at lower quantum energies could be calculated from this.

The electric field was applied to the crystal by a number of 300 v dry cells, while the current was measured by a direct-coupled feedback amplifier whose first stage (CK5889) was mounted near the crystal. An input resistor of 10^{12} ohms could be employed, and currents of 5×10^{-15} ampere were readily measurable. With this input resistor the time constant of the system was about 2 seconds.

In all the photocurrent measurements, the exposure of the crystal to light, when the electric field was applied, was kept as small as possible in order to minimize the formation of space-charge fields. The light was allowed to fall on the crystal in single "pulses" varying from 0.05 to about 5 seconds depending on the sensitivity (and hence response time) of the apparatus. Aside from the prevention of space-charge formation, the use of short pulses of light was desirable because of the poor long-term stability of the carbon arc and the effect of prolonged ultraviolet radiation on the photoconductive response (Sec. 3.4).

Absorption spectra were measured with a Beckman Model DU quartz spectrophotometer using the point-by-point method.

Where a specimen is designated "x-rayed," an exposure to the beam from an x-ray tube with a tungsten target and beryllium window is implied. The samples were placed about 8 cm from the target and the tube was operated at 50 kv and 15 ma. During the x-irradiation the specimens were covered with aluminum foil to protect them from optical radiation.

2.4 Calculation of the Data

Absorption data are presented in terms of the absorption coefficient, K, defined by

$$I = I_0 e^{-Kd}(1-R)^2,$$

where I_0 and I are the incident and transmitted intensities, respectively, d is the specimen thickness, and R is the reflection coefficient. The above expression allows for the losses at the first and second partial reflections only. Since R is small, this approximation is sufficiently accurate for our purposes. R was calculated from the index of refraction data of Strong and Brice,[10] which was extrapolated into the short-wavelength region by using the Sellmaier equation,[11]

$$\mu^2 = 1.945\lambda^2/(\lambda^2 - 1.251\times 10^6),$$

where μ is the index of refraction and λ the wavelength expressed in A.

In order to make clear the manner in which the photoconductivity data were plotted, the following simple analysis is presented:

Consider a crystal with an absorption coefficient $K(E)$, where E designates the quantum energy. K may be a composite coefficient which defines the total absorption, at a given energy, due to several different absorption processes, $K_i(E)$, i.e., $K = \sum_i K_i(E)$. If the crystal absorbs a fraction, a, of the incident radiation, the fraction absorbed by optical transitions of type i is $K_i a/K$. Let p_i be the probability that such a transition leads to a free charge carrier. Then the fraction of the incident radiation which produces free charge carriers, by all possible types of transitions, is $(a/K)\sum_i p_i K_i$. Let the carriers move an average distance x_i in unit field (we use the subscript here to allow for the possibility that both electron and hole excitation occur at the same energy, i.e., x_i takes on one of two possible values). Then each contributes a charge $x_i Ve/w^2$ to the external circuit, where w is the distance between the electrodes and V is the applied voltage. Then if N quanta/sec fall on the crystal, the observed photocurrent is

$$i = (NaeV/Kw^2)\sum x_i p_i K_i,$$

or

$$\sum x_i p_i K_i = (i/N)(K/a)(w^2/eV) \equiv Y.$$

K was determined by optical absorption measurements on each crystal and a calculated therefrom. Thus, from a combination of optical absorption and photoconductivity measurements, the quantity $Y(E)$ could be determined.

It should be observed that the photoconductive yield Y as defined above is essentially the ratio of photocurrent to incident light intensity, multiplied by a correction factor, K/a. The correction factor allows for the light which may be lost (insofar as the production of free carriers is concerned) by one or all of three important processes, *viz.*, transmission through the sample, reflection from the sample, and absorption by processes which do not lead to conductivity ($p=0$). An example of the importance of the correction factor is given in Sec. 3.5.

2.5 Sign of the Charge Carriers

Whenever a photocurrent is detected and a photoionization process thus revealed, it is always desirable to know whether the current is carried by electrons or by holes. Most of the methods which allow this determination for semiconductors do not apply to good insulators, although Yamaka and Sawamoto[9] have employed the Hall effect for this purpose. Day[5] devised a method which depended on the direction of displacement of an optically activated region of a crystal when the activation was performed, first with no applied electric field, then with the field applied. It is believed that the results of this technique are subject to misinterpretation as explained later in this section. For this reason a somewhat different method was employed in this work.

The method depends upon the asymmetry of the electric field distribution within a crystal when a space-charge field has been set up by the flow of carriers and carriers are subsequently allowed to flow in this space-charge field only. That space fields can be readily observed and maintained in MgO is shown in Sec. 3.2. It is also shown in that section that the assumption that a negligible fraction of the excited charge passes through the electrodes is in agreement with experiment. Consider the experimental situation as illustrated by Fig. 2(c) wherein the ZY planes constitute the electrodes of a with the light beam incident on the XZ plane and crystal illuminating a fraction of the volume, b wide as shown in the figure. Assuming that the distance moved by each excited carrier before trapping is small compared to either a or b, the result of an irradiation, during which the electric field is applied, is to give the field distribution shown by the solid line in Fig. 1(a). The dotted line shows the field before irradiation, i.e., that which would be calculated from the applied voltage and the electrode separation.

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[10] J. Strong and R. T. Brice, J. Opt. Am. **25**, 207 (1935).

[11] F. A. Jenkins and H. E. White, *Fundamentals of Physical Optics* (McGraw-Hill Book Company, Inc., New York, 1937), p. 294.

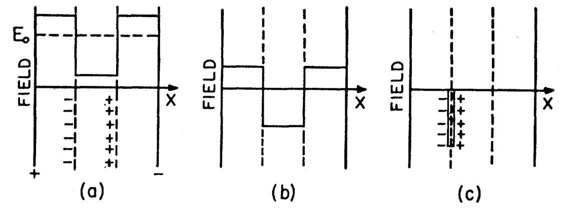

FIG. 1. Idealized electric field profiles, illustrating the method of determining the sign of the charge carriers. The crystal lies between two electrodes represented by solid vertical lines and is illuminated in the central region bounded by the dotted vertical lines; (a) shows the field profile after irradiation with a voltage applied such that the initial field is E_0, (b) is the same profile after removal of the external voltage, while (c) shows the profile after a subsequent irradiation with the two electrodes held at the same potential. The space-charges shown are for the case that the carriers are electrons.

The second step in this idealized experiment is to remove the applied voltage and bring the electrodes to the same potential. The field distribution is then as shown in Fig. 1(b) which is simply a vertical displacement of the previous diagram.

For definiteness it is assumed at this point that the excited carriers are electrons. (The discussion can be easily altered to fit the case of hole excitation.) The field distributions of Figs. 1(a) and (b) are then the result of the space-charges indicated on Fig. 1(a). The important fact here is that the electron excess lies outside the illuminated region while the electron deficiency lies within this region.

The third step of the experiment consists in the excitation of more carriers (within the same volume as previously irradiated) and their motion under the influence of the space-charge field alone. Under these conditions the motion of the excited electrons is to the right and the tendency is for the former electron deficiency to be neutralized and a new deficiency to form at the left-hand side of the irradiated region. (Notice that the electron excess is not disturbed because it lies outside the irradiated region.) If this process could be carried to completion, the space-charge distribution would be as shown in Fig. 1(c) with the corresponding electric field having an appreciable value only at the left hand edge of the illuminated region. If the photocurrent were carried by holes rather than by electrons, the "dipole" layer would exist at the opposite edge of the illuminated region (i.e., the edge nearest the electrode which was held negative during the first step of the experiment).

According to the foregoing discussion the sign of the charge carriers can be determined if the dipole layer can be located. This can be done in practice by moving a narrow beam of light across the crystal and measuring the photocurrent as a function of the beam position. If the electrodes are at the same potential during this "scanning," the photocurrent observed will be due to the motion of carriers in the previously developed space-charge field and hence will be a measure of this field. The measured dependence of photocurrent on beam position will, of course, be a true representation of the electric field distribution only if the sensitivity of the crystal is uniform: that is, if the ultraviolet irradiation has not appreciably activated the crystal. This condition very likely cannot be met in practice, but nevertheless this effect does not interfere with the location of the dipole layer.

In an actual experiment the results may be expected to deviate from those shown schematically in Figs. 1(a) to (c). There are several obvious reasons for this: (a) the carrier range may not be small compared to the width of the irradiated region, (b) the carrier range may vary during the course of the experiment by means of the activation effect mentioned above and also because the electric field is not constant during the experiment, (c) the term, "range," as used above should actually read "mean range" since the displacement of a given electron can vary between zero and a distance comparable to the distance between the electrodes, (d) the width of the scanning beam is not negligible compared to the width of the irradiated region, and (e) it is difficult to estimate the optimum duration of the second irradiation (no applied field). If insufficient time is employed, the field due to the dipole layer may be masked by that due to the un-neutralized charges at either edge of the illuminated region. If the second irradiation is prolonged to avoid the former effect, the dipole itself may be destroyed, by the continuous dark current for example.

In spite of the above-listed difficulties, it is believed that the method may be used to determine the sign of the charge carriers excited under various conditions. For, even if a clearly defined field maximum, corresponding to the "dipole" of Fig. 1(c), cannot be discerned, the location of the "dipole" can be deduced from the asymmetry of the field distribution. Examples of the use of this method are given in Secs. 3.3 and 3.5.

In the method of Day the irradiation is of necessity performed with the electric field applied. Thus, the electric field within the crystal becomes distorted by space-charge and a subsequent scan of the crystal with a beam of longer wavelength results, not in a profile of photosensitivity (implicitly assumed in Day's method), but in a profile of the product of photosensitivity and electric field. It seems, therefore, that the method may lead to incorrect results unless the effect of the space-charge is considered.

3. RESULTS

3.1 General Features of the Photoconductivity

In untreated crystals the photocurrent was found to be proportional to the electric field up to about 6000 volts/cm. In this range of fields, the dark current was negligible, i.e., less than 10^{-15} ampere. However, for fields greater than some critical value (about 6000 volts/cm), the dark current rose sharply to 10^{-14} ampere or more. This current was sufficiently unstable that photoconductivity measurements were impossible.

Usually, the photocurrents were small enough at full light intensity to prevent an investigation of the dependence of current on intensity. However, because of the larger currents available it was possible to perform the experiment on an x-rayed crystal, using 2.3-ev quanta. In this case, the photocurrent was proportional to intensity for a 40 to 1 variation of intensity. Because of the irregular spectral output of both the carbon arc and the mercury arc, it is believed that any significant deviations from proportionality in the cases of other types of crystals would have led to corresponding irregularities in the calculated yield curves. Since the latter irregularities were not observed, we conclude that in the range of intensities used (at least 1000 to 1) the photocurrent was proportional to light intensity.

The photocurrent was in all cases rather small so that the possibility that a surface effect was being observed had to considered. In order to check on this point, the following experiment was performed. The photoconductive yield of a thick (≈ 1 cm) specimen was measured. A section was cleaved off and the remainder remeasured. This procedure was repeated several times, measuring the yield at each step. Although it was impossible to obtain a specimen sufficiently homogeneous to be completely satisfactory for this experiment, the yield calculated at each step was essentially independent of thickness as should be found. The deviations from constancy which were obtained were random and not explainable in terms of a surface effect.

3.2 Development of Space-Charge

As explained in Sec. 2.3 the exposure of the crystal to light was held to a minimum in order to prevent the formation of space-charge fields. In order to demonstrate the development of such fields, the following experiment was performed.

With an electric field applied to a crystal, a portion of the volume between its electrodes was irradiated with 4.4-ev quanta and the photocurrent measured as a function of time. At intervals the electric field was removed, the electrodes were brought to the same potential, and the photocurrent measured under this condition. Figure 2(a), curve *A* shows the variation with time of irradiation of the photocurrent with applied field, while curve *B* gives the current when measured with no applied field. The photocurrents of curve *B* flow in the opposite direction to those in curve *A*.

The irradiation was then continued with no applied electric field (electrodes connected) and the photocurrent was measured as a function of time. At intervals the electric field was applied and the photocurrent was measured under this condition. The corresponding curves are presented in Fig. 2(b). In each case curve *C* is the sum of curves *A* and *B*.

The results of the foregoing experiment are consistent with the following assumptions which are reasonable in any case:

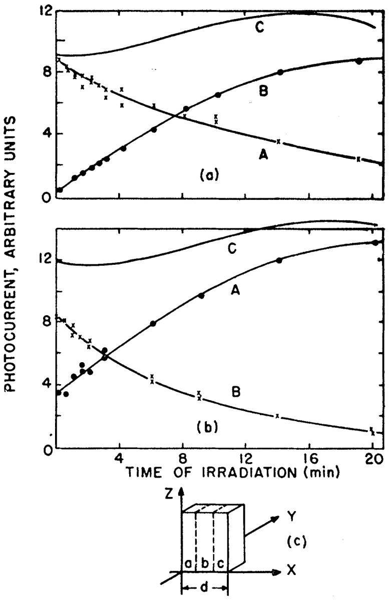

FIG. 2. Development and removal of space-charges by optical irradiation. (a) Irradiation with electric field on, *A* measured with field on, *B* with field off. (b) Irradiation with field off, *A* measured with field on, *B* with field off. In both cases the currents of *A* and *B* flow in opposite directions and *C* is the sum of the absolute values of *A* and *B*. (c) Geometry of the experiment. The electrodes lie in *YZ* planes and the light beam travels parallel to the *Y* axis. The irradiated region lies between the dotted lines.

(a) the mean range of the charge carriers is small compared to the distance between the electrodes and to the width of the irradiated region;

(b) the amount of charge which passes through the electrodes is negligible;

(c) carriers are lost by trapping in states from which their release time is large compared to the duration of the measurement.

If the above assumptions hold, then the net result of the experiment is to remove a sheet of charge from one side of the irradiated region[12] and to place it at the other. We consider, for example, the situation at *T*, the instant at which the curves of Fig. 2(a) intersect. At this instant the electric field in the irradiated region is reduced to one-half its initial, known, value and the charge in the sheets may, therefore, be calculated from Poisson's equation. The sheet charge may also be calculated by integrating the external photocurrent up to time *T*. For the experiment of Fig. 2 the values calculated in these two fashions differed by 4%, well within the experimental error.

It is also easily shown that under the above assumptions the sum of the absolute values of the currents measured with and without the applied electric field give the true no-space-charge value of the photocurrent. This would imply that curve *C* of Fig. 2 should be a horizontal line. However, it is shown in Sec. 3.4 that such prolonged exposure to ultraviolet light increases the photoconductivity, probably because of trap-filling. Consequently, the sum of curves *A* and *B* is expected to increase with time as observed. It should be noted, however, that this does not influence the calculation of the sheet charge, when the calculation is performed as outlined above.

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[12] H. Kallmann and B. Rosenberg, Phys. Rev. **97**, 1596 (1955).

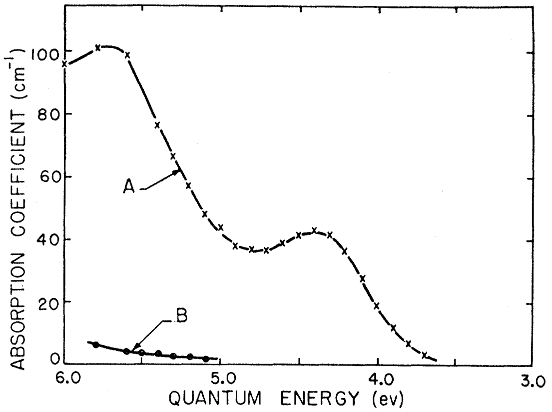

FIG. 3. Typical absorption spectra before any treatment. Spectra such as B could be obtained from A by heating the specimen in vacuum.

3.3 Untreated Crystals

Most of the specimens, as obtained, showed an ultraviolet absorption spectrum consisting of two obvious bands (Fig. 3, curve A). Those which did not, showed a spectrum as shown by curve B. The actual magnitude of the absorption varied considerably from crystal to crystal but these two shapes were always found. Spectra like curve A have been shown[1] to consist of three bands, centered at 4.3, 4.8, and 5.7 ev.

The photoconductivity spectrum of crystals characterized by absorption spectra of either type A or type B (Fig. 3) were as shown in Fig. 4. Variations from crystal to crystal as far as the shape of the spectrum is concerned, occurred mainly in the energy region above 5 ev. For some specimens the yield continued to rise after a slight inflection at about 5 ev. Below 5 ev, however variations in shape were minor. Indeed, it was found that over part of the energy region the spectrum was well represented by a Gaussian-shaped band centered at 5.05 ev. The nature of the fit is also shown in Fig. 4. In the subsequent discussion we consider the yield in the vicinity of 5 ev as being due to the 5-ev band.

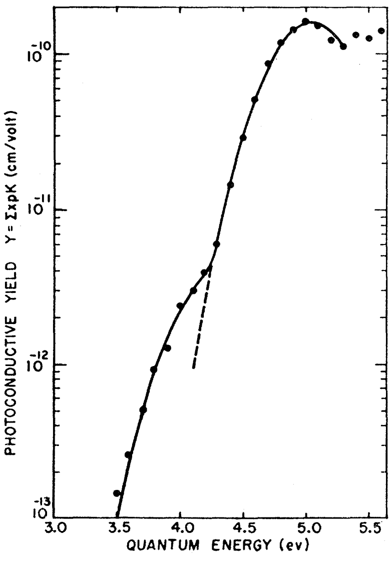

FIG. 4. A typical photoconductive yield curve before any treatment of the specimen. The solid curve at high energies, becoming a dotted line at somewhat lower energies, is a Gaussian centered at 5.05 ev.

Variations in the magnitude of this band were not very great. Table II shows the magnitude of the yield at 4.6 ev for a selection of crystals. Also indicated is the type of absorption spectrum found for each, classified according to Fig. 3. It may be seen that there is no correlation between the magnitude of the 5-ev band and the presence or absence of the 4.3-, 4.8-, and 5.7-ev bands. Neither was any other feature of the photoconductive yield connected with this particular property of the crystals.

Considering that the measured 5-ev yield depends both on the density of photoionizable centers and on the range of the free carriers (which is itself determined by the density of trapping centers), it is perhaps surprising that the magnitude of the yield does not show a greater variation from crystal to crystal. There are at least two possible reasons for this, *viz.*, (1) the impurity responsible for the 5-ev band may be one of those whose concentration was found[2] to vary little among specimens, and (2) an important range-limiting (traping) mechanism may be contributed by the photoionizable center itself. In the former case the concentration of trapping centers would also be required to vary little among specimens. In the latter case, however, if n is the density of ionizable centers, we have $K\sim n$ and $x\sim 1/n$ so that $Y\equiv xpK\sim p$ and is therefore independent of the density of centers. Since the yield is not strictly constant among specimens, we are compelled to postulate either the first possibility above or a mixture of both possibilities. It will later be argued (Sec. 3.6) that the latter is more likely for the specimens measured in this work.

TABLE II. Photoconductivity at 4.6 ev for a selection of MgO crystals.

xpK at 4.6 ev (10^{-11} cm/volt)	Type of absorption spectrum (Fig. 3)	xpK at 4.6 ev (10^{-11} cm/volt)	Type of absorption spectrum (Fig. 3)
14.8	B	4.4	B
6.0	B	6.3	B
2.5		5.4	A
7.1	B	3.4	A
3.8	B	4.1	A
6.0	B	4.6	B
5.7	A	4.5	B
4.9	A	5.0	B
17.7	B		

The sign of the charge carriers produced by irradiation in the 5-ev band was determined by the method described in Sec. 2.5. In this case the irradiations were performed at 4.4 ev. The field distributions at various stages of the process are shown in Fig. 5. After the second and third irradiations, the location of the maximum field intensity is seen to be shifted towards the electrode which was positive during the first (applied field) irradiation. According to our interpretation the charge carriers are therefore negative.

Further discussion as to the nature of the 5-ev center will be given in a later section. For the present we summarize the conclusions and postulates of this section in two equations describing the photoionization of the 5-ev center and two alternative trapping mechanisms.

$$\begin{aligned} &A^{n}+h\nu(\text{5-ev band})\rightarrow A^{n+1}+e,\\ &A^{n}+e\rightarrow A^{n-1}, \qquad\qquad (1)\\ &B^{m}+e\rightarrow B^{m-1}. \end{aligned}$$

In the foregoing, the photoionizable 5-ev center is designated as imperfection A having a positive charge ne while all other imperfections capable of trapping electrons are lumped into B (m and n are integers).

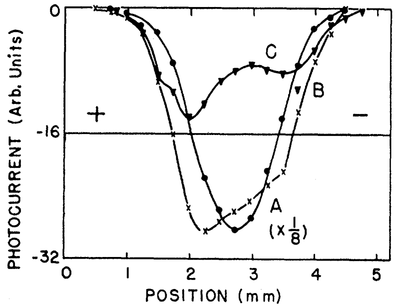

FIG. 5. Electric field distributions obtained in the determination of the sign of the charge carriers excited by 5-ev band irradiation (4.6 ev). All currents were measured with the crystal electrodes held at the same potential, A after irradiation with applied electric field, B after a subsequent irradiation with no applied field, and C after further irradiation with no applied field. A has been reduced vertically to $\frac{1}{8}$ to accommodate it on the same scale as the other two curves. The signs indicate the polarity of the electric field during the initial irradiation.

The sign of the charge carriers excited in the 4-ev region was determined as above except that this time the irradiating energy was 3.8 ev. The corresponding field distributions are shown in Fig. 6. Here the field maximum shifts towards the originally negative electrode upon the second irradiation and hence the carriers are, according to our interpretation, holes.

3.4 Effect of Optical Irradiation

Prolonged irradiation by quanta which are capable of exciting charge carriers may be expected to change the photoconductivity and absorption spectra.[5,7,13] The charge carriers can be trapped by the photoionizable centers themselves or by other shallower levels, in either case giving rise to types of centers not present before the irradiation. The changes which are occasioned by the prolonged irradiation may, of course, be expected to depend upon the sign of the carrier excited. Therefore, these experiments offer a means of testing one conclusion of Sec. 3.3, *viz.*, that either holes or electrons may be excited in normal crystals depending upon the wavelength of the irradiation.

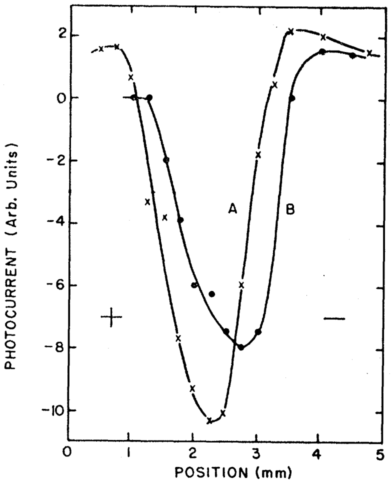

FIG. 6. Electric field distributions obtained in the determination of the sign of the charge carriers excited in the energy region lying below the 5-ev band. All currents were measured with the crystal electrodes held at the same potential, A after irradiation (3.8 ev) with applied electric field, B after a subsequent irradiation with no applied field. The signs indicate the polarity of the electric field during the initial irradiation.

Figure 7 shows the effect on the photoconductivity of irradiations in the 5-ev band and in the 4-ev region. The absorption change brought about by the 5-ev irradiation has the same shape as curve A of Fig. 3 with an increase in absorption coefficient at 4.3 ev $\Delta K=1$ cm^{-1}. The total irradiation was 4×10^{17} quanta/cm^{2}. Irradiation in the 4-ev region resulted in a barely measurable increase in the ultraviolet absorption. Nothing specific could be determined about this increase, but was definitely not of the nature produced by the higher energy irradiation.

It seems reasonable to conclude from the above noted differences in the effect of irradiation in the 4- and 5-ev regions that different charge carriers are involved in

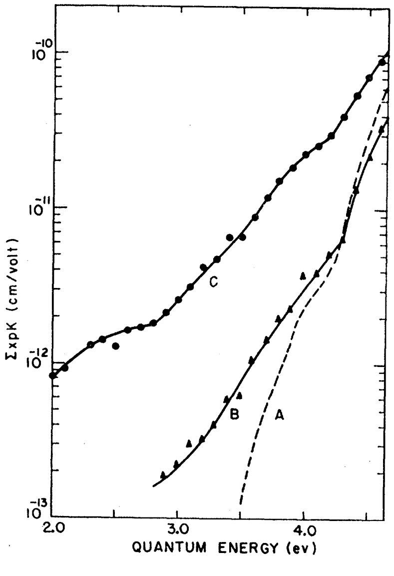

FIG. 7. The effect of optical irradiation on the photoconductive yield. A, untreated crystal; B, irradiated with 3.8-ev quanta (1.6×10^{19} cm^{-2}); C, irradiated with 4.6-ev quanta (4×10^{17} cm^{-2}).

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[13] J. H. Hibben, Phys. Rev. **51**, 530 (1937).

the two regions. This, of course, is consistent with our previously quoted direct determination of the sign of the charge carriers.

The enhancement of photoconductivity by irradiation in the 5-ev band is believed to be due to centers formed by the trapping of electrons released by the enhancing irradiation. The interpretation is the same as that given by Day[5] who performed the irradiation at 4.0 ev and obtained an enhanced spectrum similar to that shown in Fig. 7, curve *C*. Day subsequently determined that the charge carriers excited by 3.7-ev quanta were holes, in agreement with our determination (Sec. 3.3). However, the conclusion[5] that the enhanced photoconductivity spectrum (Fig. 7, curve *C*) is therefore due to trapped holes is believed to be in error, since as outlined above the change from 4.0 ev to 3.7 ev would be sufficient to change from predominantly electron excitation to predominantly hole excitation.

The enhanced spectrum obtained by irradiation in the 5-ev band is the same as is also obtained after the x-irradiation and partial thermal decay of crystals at room temperature. Consequently the further discussion of this spectrum will be deferred to the next section.

The absorption change brought about by 5-ev band irradiation, *viz.*, development of the 4.3-, 4.8-, and 5.7-ev absorption bands, implies a close relation between these transitions. We now present a model which is in accordance with the experimental results. This model has already been employed by Soshea, Dekker, and Sturtz[1] to explain their extensive results on x-rayed crystals.

None of the three absorption bands (5.7, 4.8, 4.3 ev) was observed in photoconductivity spectra, even in cases where they dominated the absorption spectrum. Consequently, it must be concluded that the probability p of thermal ionization of the excited states is considerably smaller than for the 5-ev band or the 4-ev region.

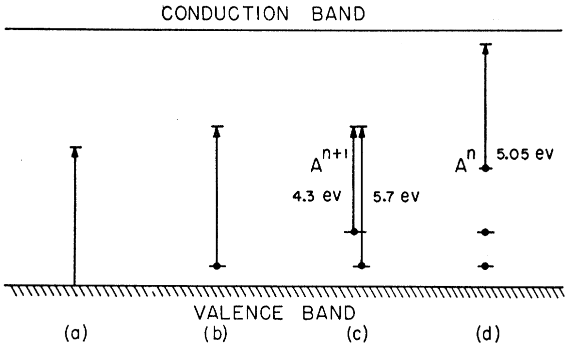

FIG. 8. (a) Partial energy level diagrams and (b) possible representations of the transitions providing the 4.3-, 4.8-, and 5.7-ev absorption bands. (c) Model of center responsible for 2 of these transitions. A^n designates an impurity ion A with charge $+ne$. (d) Proposed origin of the 5-ev transition observed in photoconductivity. The ion A^n is identified as Fe^{2+} in the text.

Since it is reasonable to expect that the excess oxygen is incorporated substitutionally as a divalent ion, the observed optical transitions thus produced may be expected to result from electronic transitions to levels which have been emptied to complete the outer shell of the ionic excess oxygen. Thus, if the transitions took place from the valence band they might be visualized as in Fig. 8(a). However, it has been argued above that the transition produces a free hole with very small probability. Hence, we visualize transitions such as that illustrated by Fig. 8(b).

It has been observed by several workers[1,4,14] that the ratio of the intensities of the 4.3- and 5.7-ev bands is strikingly constant under rather widely varying conditions, while the 4.8-ev band has a different intensity relative to the other two, depending on the conditions of formation of the bands. These facts strongly suggest that the 4.3- and 5.7-ev transitions occur in the same center while the 4.8-ev transition may be characteristic of a different center. The experimental evidence would still require, however, that circumstances which would produce the one type of center would also produce the other. The transitions which are visualized as giving rise to the 4.3- and 5.7-ev absorption bands are shown in Fig. 8(c).

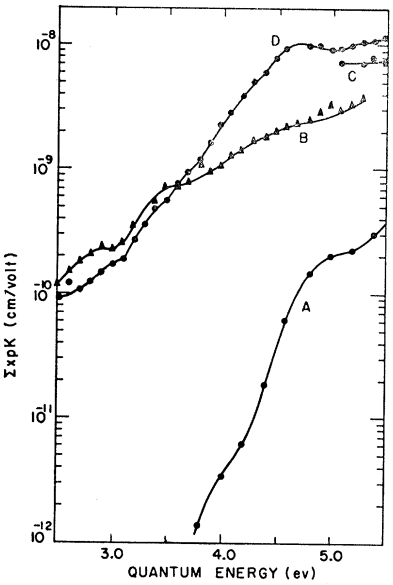

FIG. 9. The effect of x-rays on the photoconductive yield. *A*, untreated crystal; *B*, after 40 min of x-irradiation; *C*, after 4 hours subsequent thermal decay at room temperature; *D*, after 50 hours decay.

Now the appearance of the 4.3- and 5.7-ev absorption bands upon prolonged irradiation in the 5-ev band is readily explained if the 4.3- and 5.7-ev bands are associated with the A^{n+1} center [see Eq. (1) of Sec. 3.3]. This still leaves the 4.8-ev transition to be accounted for. Since the latter is apparently developed during the single reaction (1) we tentatively assign it also to A^{n+1} with perhaps somewhat different surroundings.

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[14] J. P. Molnar and C. D. Hartmann, Phys. Rev. 79, 1015 (1950).

3.5 Effect of X-Ray Irradiation

Figure 9 shows the enhancement of photoconductivity obtained by exposure to x-irradiation. The absorption spectrum before the irradiation was of the type exemplified by Fig. 3, curve *B*, while that after the irradiation contained the 5.7-, 4.8-, and 4.3-ev bands as well as additional absorption in the visible region of the spectrum. Changes of this nature in the absorption are discussed by Soshea *et al.*[1] It may be observed that after the end of the irradiation there was a rather rapid change in the shape of the photoconductivity spectrum. The shape represented by curve *D*, however, was maintained thereafter. It should be noted that this shape is similar to that obtained by optical irradiation in the 5-ev band (Fig. 7) and is therefore probably due to a single sign of carrier over the whole energy range. By the method previously described it was determined that the carriers were electrons (Fig. 10) in agreement with the previous conclusion concerning the carriers excited by 5-ev band radiation.

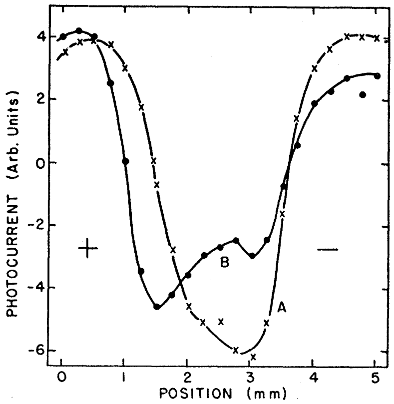

Fig. 10. Electric field distributions obtained in the determination of the sign of the charge carriers excited in a specimen such as that represented by curve *D* of the previous figure. All currents were measured with the crystal electrodes held at the same potential, *A* after irradiation (4.4 ev) with applied electric field and *B* after further irradiation with no applied electric field. The signs indicate the polarity of the electric field during the initial irradiation.

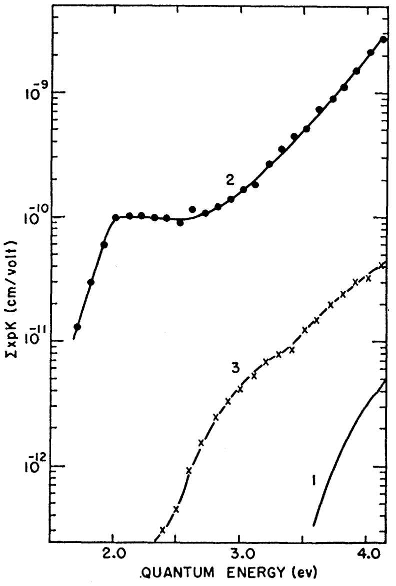

Fig. 11. The effect of crystal temperature during x-irradiation on the enhancement of the photoconductive yield. 1, untreated crystal; 2, x-rayed at room temperature; 3, x-rayed at 260°C. All spectra were measured at room temperature.

The more stable shape of the enhanced photoconductivity spectrum is shown over a wider energy range in Fig. 11, curve 2. At energies lower than about 3.5 ev this is the same as that obtained by Day,[5] both by 5-ev band irradiation and by neutron bombardment. This spectrum should be compared with that obtained by x-irradiation at a higher temperature (Fig. 11, curve 3). The low-energy photoconductivity was not obtained in the latter case implying that the centers in question were not stable at the temperature involved. More important, however, is the fact that the shape of the spectrum at higher energies was unchanged. This implies that the higher energy photoionization is principally due to a single type of center. This conclusion is further supported by the observation that optical irradiation of a crystal x-rayed at 260°C did not show any selective bleaching of the photoconductivity at the energy of irradiation (3.25 ev). Indeed, the effect of the irradiation was to fill the shallow (optical ionization energies <2.5 ev) traps and thus enhance the photoconduction in the higher energy region by a factor which was independent of energy.

According to the above arguments we classify the electron traps into two groups, *viz.*, those evidenced by the low-energy (<2.5 ev) photoconductivity and those which supply the photoconductivity above this energy. There is some reason for believing that the low-energy photoionization is supplied by more than one type of center: (1) Yamaka[8] detected a number of traps whose thermal ionization energies were estimated to fall in the region 0.56 to 1.58 ev. Since these traps were apparently filled either by x-irradiation or by ultraviolet irradiation in the 5-ev band they are, according to the present interpretation, electron traps. Some of these would presumably have optical ionization energies lying in the range in question. (2) The complex thermal decay at room temperature of the x-ray induced absorption implies the presence of several shallow electron traps. This is discussed in more detail by Soshea, Dekker, and Sturtz.[1]

Day[5] measured photoconductivity in neutron-irradiated MgO and reported two bands introduced, one at 3.6 the other at 4.8 ev. Since the excitation was in that case believed to be at least partially electronic, we looked for these bands in x-rayed crystals. According to the data already presented, no bands were found at these energies. However, when the measurements were repeated on an x-rayed specimen which was about 1 cm thick in the direction of the light beam (this is about the thickness used by Day) the results shown in Fig. 12

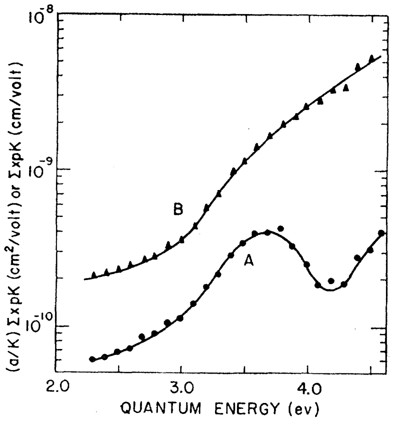

FIG. 12. Curves illustrating the importance of the correction factor, K/a, in determining the true shape of the photoconductive yield curve for an x-rayed crystal. A, $(a/K)\Sigma xpK$ (i.e., uncorrected ratio of photocurrent to light intensity); B, ΣxpK (i.e., corrected ratio).

were obtained. Here, curve A is essentially the ratio of photocurrent to light intensity, while in curve B the correction K/a from Sec. 2.4 has been applied. It is evident that the peak at 3.6 ev in the apparent yield is removed by the application of the correction factor, which itself peaks at 4.3 ev.[1] Although the measurements were not extended that far, a similar result would undoubtedly have been obtained at 4.8 ev since a minimum in the optical absorption (and hence in the correction factor) occurs at this energy (Fig. 3). The spurious peaks were not obtained in the uncorrected yield curves of thinner crystals because of the manner in which the thickness enters into the expression for the correction factor.

3.6 Crystals Doped with Iron

Crystals containing higher concentrations of certain impurities than found in normal crystals were obtained from the General Electric Company, Cleveland.[15] These were grown from a melt doped with an oxide of the desired impurity.

Figure 13, curve 1, shows the photoconductivity spectrum of a specimen containing approximately 0.4 atomic percent of iron. The magnitude of the 5-ev band is somewhat greater than found in most normal crystals. This implies that the A^n center may be associated with some valence state of the iron impurity. On the other hand, the magnitude of the 5-ev band is not as great as might be expected simply on the basis of the increase in iron concentration and indeed is not as great as in some undoped crystals. However, according to the discussion of Sec. 3.3, if A^n is one of the principal trapping centers the photoconductive yield from A^n tends to be independent of the concentration of A^n. Thus, it is still possible that the A^n center is associated with some valence state of the iron impurity.

Now, according to the electron spin resonance measurements of Wertz[16] and the optical absorption measurements of Haxby[2] the 5.7- and 4.3-ev absorption bands may be associated[1] with the center Fe^{3+}. In Sec. 3.3 we have associated these bands with A^{n+1}. Thus, we deduce that the 5-ev band ionization (A^n) is due to the center Fe^{2+}.

It has been postulated in the above that the Fe^{2+} center is itself the principal electron trap. Thus, it is interesting to attempt to associate a portion of the enhanced photoconduction in x-rayed crystals with the filled trap, Fe^{+}. There seems to be no direct evidence available on this point but if we assume that Fe^{+} accounts for at least some of the photoconduction at low energies (Fig. 11, curve 2), then one hitherto unexplained fact can be understood. Haxby[2] has shown that in contrast to crystals of normal purity,[1] the x-ray-induced absorption in iron-doped specimens decays to zero at room temperature. This implies that such crystals contain a preponderance of *shallow* trapping levels and it therefore seems reasonable to associate these levels with the dominant impurity, *viz.*, iron.

A comparison of Fig. 13, curve 2 and Fig. 11, curve 2, shows that the x-ray enhancement of photoconductivity is greatly inhibited by the presence of the greater concentration of iron. This result is to be expected on the basis of our previous arguments, for the specimen in the state corresponding to curve 1 of Fig. 13 showed no ultraviolet absorption bands and therefore contained all its iron as Fe^{2+}. Thus, the electron range was much lower than normal and remained lower even after x-raying because, as Haxby[2] has shown, less of the iron is converted to Fe^{3+}. Thus, the large enhancement of photoconductivity (Fig. 11, curve 2), previously shown to be due to electrons, was not observed.

CONCLUSIONS

The main conclusions to be drawn from this work are listed below.

(1) All MgO crystals measured show a Gaussian-shaped absorption band centered at 5.05 ev (Sec. 3.3). This band is usually not detected in optical absorption measurements because it occurs in a region of the spectrum where absorption by other mechanisms is dominant. It is readily detectable in photoconductivity measurements, however, presumably because the excited state of the corresponding center is readily ionized by thermal energy. The thermal process results in an electron in the conduction band. The 5-ev transition was shown to be closely related (Sec. 3.4) to a center which shows three ultraviolet absorption bands (5.7, 4.8, and 4.3 ev) but no corresponding photoconductivity. The latter center seems to be identifiable[2,16] with the impurity Fe^{3+} and through the relation just mentioned, a correspondence between the 5-ev transition and the impurity Fe^{2+} is deduced.

(2) The Fe^{2+} center acts as an electron trap for optically excited carriers. This conclusion is based on the observation that the magnitude of the 5-ev band is

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[15] We are indebted to the Advanced Lamp Development Laboratory of the General Electric Company, Cleveland, for their cooperation in supplying specimens doped with various impurities.

[16] J. E. Wertz and P. Auzins, Phys. Rev. **106**, 484 (1957).

relatively insensitive to the concentration of iron and to the proportion of the total iron which is in the form Fe^{2+}. The filled trap (Fe^{+}) is believed to be responsible for at least some of the low-energy (<2 ev) photoconductivity observed in x-rayed crystals (Sec. 3.6). The association with the *low*-energy photoconductivity in such crystals is based on the observation of Haxby[2] that the x-ray-induced absorption in iron-doped crystals decays thermally as though they contain a preponderance of *shallow* electron traps.

(3) Optical irradiation at energies near 4.0 ev excites free holes. The transitions involved have not yet been associated with a specific impurity.

(4) Crystals of normal purity contain impurities other than Fe^{2+} which can act as electron traps. These show up as an enhanced photoconductivity above about 2.5 ev in x-rayed specimens.

(5) There is no evidence for bands of photoconductivity at 3.6 and 4.8 ev in x-rayed specimens. The apparent bands at these energies reported by Day[5] are believed to be due to intense non-ionizing absorption at 4.3 and 5.7 ev.

DISCUSSION

Clarke[7] has concluded that the 4.3-, 4.8-, and 5.7-ev bands are due to positive holes trapped at lattice inhomogeneities. This is in contradiction to the conclusions of this paper which deduces that the absorption bands in question are associated with holes which have been trapped by Fe^{2+} ions. Clarke arrived at his conclusion by a process of elimination in which the possibility of hole trapping by Fe^{2+} was removed from consideration by a comparison of the thermal stabilities of "holes trapped at iron or chromium ions"[17] and the "excess oxygen bands." The experimental evidence is that, although the number of Fe^{3+} ions decreases rapidly when x-rayed or ultraviolet-irradiated specimens are heated at 600°C, the 4.3-, 4.8-, and 5.7-ev bands in unexcited crystals are stable against such a heat treatment. It is believed that this argument is not legitimate when one considers the principal result of Sec. 3.4, *viz.*, that the ultraviolet irradiation employed by Clarke and by Day lay in the 5-ev band and in fact, results in trapped *electrons* and not in trapped holes as previously supposed. The stability of the absorption bands formed by ultraviolet excitation is then determined not by the stability of the corresponding center but rather by the stability of the trapped electrons. Consequently the bands would be expected to be stable in the absence of trapped electrons as is the case when the absorption is the result of nonstoichiometry.

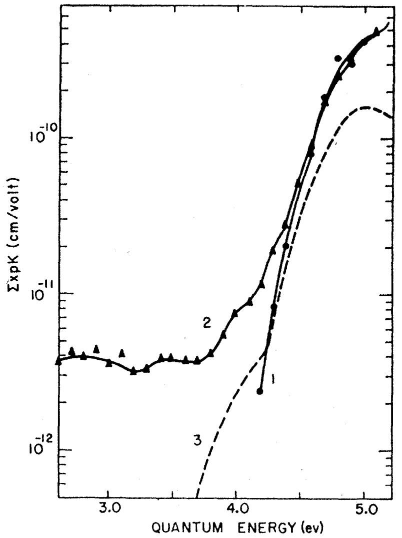

FIG. 13. The effect of x-irradiation on the photoconductive yield of a specimen of high iron content. 1, before x-irradiation; 2, after x-irradiation. 3 is a typical curve for an untreated specimen of normal purity.

ACKNOWLEDGMENTS

The author is indebted to Professor A. J. Dekker and Professor W. G. Shepherd for advice and encouragement and to B. V. Haxby, R. G. Lye, and R. W. Soshea for many helpful discussions. W. D. McNeil performed many of the measurements and calculations.

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[17] F. P. Clarke, Phil. Mag. 2, 621 (1957).