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U Center in Potassium Bromide*†

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The absolute quantum efficiency for the destruction of *U* centers and the formation of anion vacancies in KBr at 78°K has been found to be 0.61 ± 0.07 when the *U* optical absorption band is bleached by 225-mμ radiation absorbed at the maximum of the *U* band. The quantum efficiency decreases significantly as the energy of the absorbed photons increases. It is suggested that the high-energy tail of the *U* band is due to a secondary band and that the quantum efficiency of this band is 61 percent of that of the primary *U* band. Previous results concerning the formation of isolated anion vacancies and interstitial hydride ions and interacting pairs of these entities are confirmed. However, the oscillator strengths of the perturbed α bands are found to be equal to that of the unperturbed α band.

INTRODUCTION

Alkali halide crystals which contain a trace of hydride ion possess an optical absorption band, the *U* band, in the ultraviolet region of the spectrum.[1,2] In KBr-KH at 78°K, the wavelength of the maximum of the *U* band is 225 mμ. The hydride ions, which are located at normal anion lattice sites of the crystal, are converted at room temperature into molecular hydrogen and *F* centers by radiation absorbed by the *U* band. The quantum efficiency of this process approaches unity above 700°K but decreases to a negligible value at 150°K. Below 150°K, the reaction products of the optical bleaching of the *U* band are anion vacancies and interstitial hydride ions.[3–5] The quantum efficiency of this process increases with decreasing temperature.[6] The interstitial hydride ions are responsible for a broad absorption band, the U_1 band, which extends in KBr from the *U* band to 320 mμ. The absorption spectrum of the anion vacancies includes the normal α band and adjacent bands that are due to anion vacancies which interact with neighboring interstitial hydride ions.[7,8] These bands are located in the spectral region between the *U* band and the fundamental exciton absorption of the crystal. The interaction of the interstitial hydride ions with the anion vacancies is also revealed by their infrared absorption spectrum.[9]

The spectral distribution of the quantum efficiency of the conversion of *U* centers into *F* centers at room temperature is puzzling in that it is not constant within the *U* band but increases with decreasing wavelength and approaches unity for radiation absorbed by the tail of the fundamental exciton band.[10] Also, between room temperature and 102°K, the photoconductivity is small for excitation within the *U* band and rises to a maximum in the wavelength region between the *U* band and the fundamental exciton band.[11,12]

The work described in this paper consisted of a measurement at 78°K of the absolute quantum efficiency of the destruction of *U* centers as a function of wavelength within and on the short-wavelength side of the *U* band. The spectral distribution of the quantum efficiency for the generation of anion vacancies was also determined. The changes in optical absorption that are the result of low-temperature optical bleaching of the *U* band and its thermal and optical restoration are described.

EXPERIMENTAL

The potassium bromide crystals were obtained from the Harshaw Chemical Company. *F* centers were introduced into the crystals by heating them in potassium vapor in a glass vacuum system. Triply vacuum-distilled potassium was used for this purpose. The *F* centers were converted into *U* centers by heating the crystals at 370°C in hydrogen at 1-atm pressure.

The optical-absorption measurements were made with a Cary Model 14R spectrophotometer which was filled with nitrogen. Slit widths were less than 0.2 mm for almost all measurements at wavelengths greater than 200 mμ. Below 200 mμ, slit widths as large as 1 mm were used.

The Cary spectrophotometer and its hydrogen lamp were also used as the radiation source for the bleaching of the *U* band during the measurements of quantum

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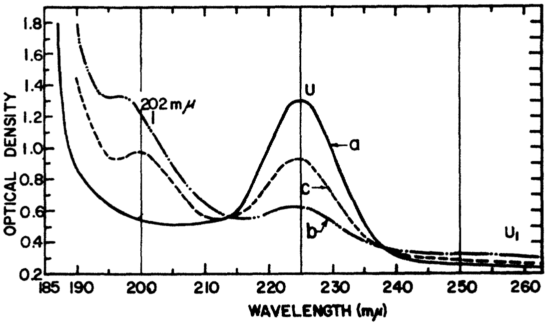

FIG. 1. a: optical absorption of a KBr-KH crystal at 78°K; b: after 225-mμ irradiation at 78°K; c: after warming the crystal to 106°K and recooling to 78°K.

efficiency. A calibrated Cs_3Sb photocell was used to determine the radiation density incident on the crystals. The optical bleaching of the U and U_1 bands was performed, however, with a small Farrand grating monochromator and Uniarc mercury lamp during the preliminary observations of the conversion of U centers into anion vacancies and interstitial hydride ions.

The crystals, which had typical dimensions of 1 cm ×1 cm ×1 mm, were mounted in a copper block in a stainless-steel Dewar which was similar to that described by Dutton and Maurer.[13] A spot of low-vapor-pressure grease on one corner of the crystal and metallic clamps ensured good thermal contact between crystal and block. The crystal temperature was measured with a Au+2.1% Co versus Ag+0.37% Au thermocouple secured with Duco cement in a hole drilled into an edge of the crystal.

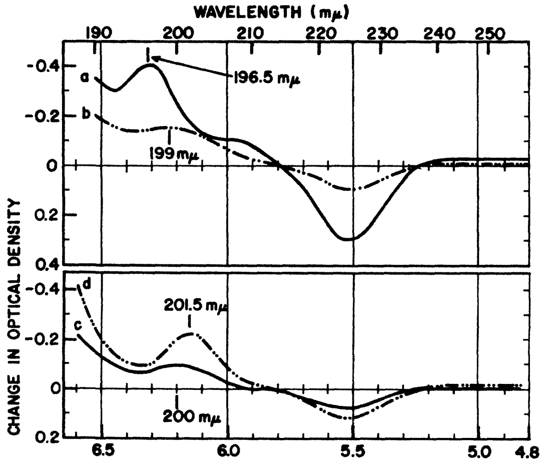

FIG. 2. Changes in optical absorption that occurred within a series of temperature intervals during heating of the crystal. At the peak temperature of each interval the crystal was recooled to 78°K for the optical absorption measurement between a: 78° and 106°K; b: 120° and 160°K; c: 160° and 200°K; d: 200° and 235°K.

The concentration n of U centers was calculated from Samakula's equation in the form

$$n = 3.55 \times 10^{15} k_m, \qquad (1)$$

where n is the number of U centers per cubic centimeter and k_m is the absorption coefficient in cm^{-1} at the maximum of the U band at 78°K, the temperature at which the absorption measurements were made. The numerical factor of Eq. (1) was derived from its room temperature value of 6.1×10^{15} by measuring the k_m of the U band in the same crystal at room temperature and 78°K. The room temperature numerical factor is consistent with an oscillator strength and half-width of the U band of 0.83 and 0.58 eV, respectively.[8] In the present experiments, the room temperature and 78°K half-widths of the U band were found to be 0.58 and 0.31 eV, respectively.

RESULTS

The optical absorption of a KBr–KH crystal at 78°K is shown by curve a of Fig. 1. The U band has its maximum at 225 mμ and the concentration of U centers is 4.7×10^{16} cm^{-3}. The result of optical bleaching at 78°K of the U band by 225 mμ radiation is shown by curve b of Fig. 1. The U_1 band has appeared on the long wavelength side of the U band while on the short wavelength side of the U band the optical absorption has increased and there has been an apparent shift of the fundamental absorption edge of the crystal to longer wavelengths. This apparent shift is probably due to the formation of the γ band which has its maximum at 189.5 mμ at 4°K.[14] This band appears to be associated with the anion vacancy. The increased absorption between 190 and 215 mμ is a superposition of several bands which include the α band of the anion vacancy at 202 mμ. Curve c of Fig. 1 shows the optical absorp-

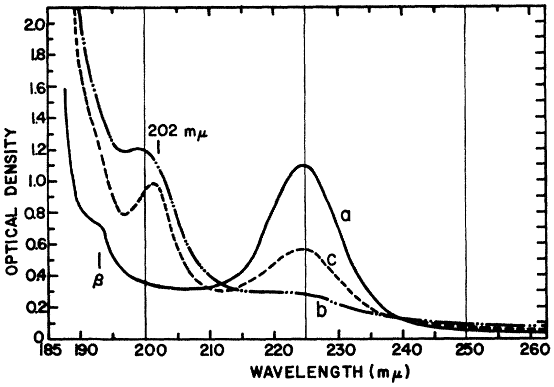

FIG. 3. a: optical absorption of KBr-KH at 78°K; b: after 225 mμ irradiation at 78°K; c: after 255 mμ irradiation in the U_1 band at 78°K, partially restoring the U band. Curves b and c show the marked change in form of the anion vacancy absorption band.

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tion at 78°K after warming the crystal to 106°K and recooling to 78°K. The U_1 band, the γ band, and a band in the vicinity of 197 mμ have partially disappeared while the *U* band has been partially restored.

The changes in optical absorption that occurred within a series of temperature intervals during heating of the crystal are shown in Fig. 2. After heating the crystal to the highest temperature of each interval, it was recooled to 78°K where the optical absorption was remeasured. Curve a of Fig. 2 shows the changes that occurred on heating the crystal from 78 to 106°K. This difference curve shows clearly that an absorption band with a maximum at 196.5 mμ disappeared during this initial heating, while about 40% of the *U* band was restored and a similar proportion of the U_1 band was lost. Curve b of Fig. 2 shows the changes that occurred between 120 and 160°K on reheating. As in the first heating to 106°K, the *U* band grew, the U_1 and γ bands decreased but the decay of a band at 200 mμ is now visible. Between 160 and 200°K, there were additional decreases in the U_1 band, the γ band, and the band at 200 mμ while the *U* band grew. These changes are shown by curve c of Fig. 2. Between 200 and 235°K, the U_1 band, the γ band, and the α band at 202 mμ disappeared. Curve d of Fig. 2, which shows these changes, yields a half-width of the α band of 0.23 eV. After heating to 235°K, the *U* band was almost completely restored; only a few percent of the *U* centers were lost and converted into *F* centers. The optical absorption of the crystal after heating to room temperature is shown by curve a of Fig. 3. The optical absorption of the crystal after heating to room temperature was essentially the same as that after heating to 235°K. The β band of the *F* centers is visible at 193 mμ.

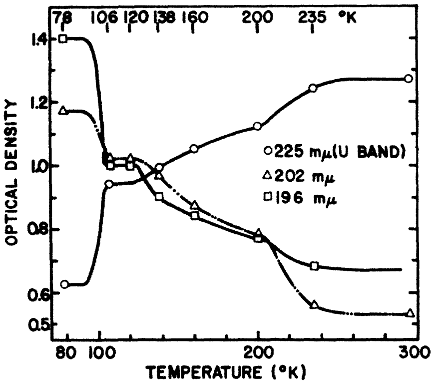

FIG. 4. Restoration of the *U* band and loss of anion vacancies on warming of the crystal from 78°K.

These observations are in excellent agreement with the results of Fujita,[7] and Timusk and Martienssen.[8] Fujita observed the displacement of the apparent alpha band on warming to higher temperatures and suggested that it was due to the recombination of nearby interstitial hydride ions with anion vacancies. Timusk and Martienssen optically bleached the *U* band at 58°K and found that three absorption bands with maxima at 6.312, 6.190, and 6.143 eV were formed. These bands disappeared after warming of the crystal to 130, 175, and 300°K, respectively. Timusk and Martienssen suggested that the two higher energy bands are due to anion vacancies which are perturbed by nearby interstitial hydride ions and that the band at 6.143 eV is the normal α band due to the unperturbed vacancy.

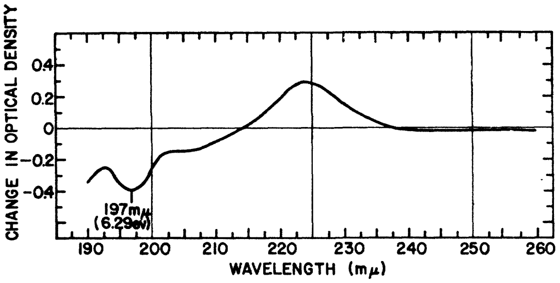

FIG. 5. Restoration of the *U* band and loss of anion vacancies as a result of 255 mμ radiation absorbed in the U_1 band at 78°K.

Figure 4 shows the changes in optical absorption at 225, 202, and 196 mμ on warming of the crystal from 78°K. More detailed observations by Fritz[9] have shown that the changes in optical absorption between 78 and 106°K take place very abruptly at 103°K.

After the heating of the crystal to room temperature, which restored the *U* band and resulted in the optical absorption curve a of Fig. 3, the *U* band was again bleached by radiation of 225 mμ wavelength. The result, curve b of Fig. 3, was substantially the same as was obtained in the original experiment which yielded curve b of Fig. 1. The *U* band was then partially restored by optical bleaching of the U_1 band with radiation of 255-mμ wavelength. As curve c of Fig. 3 shows, the partial bleaching of the U_1 band was accompanied by a partial restoration of the *U* band, and a decrease

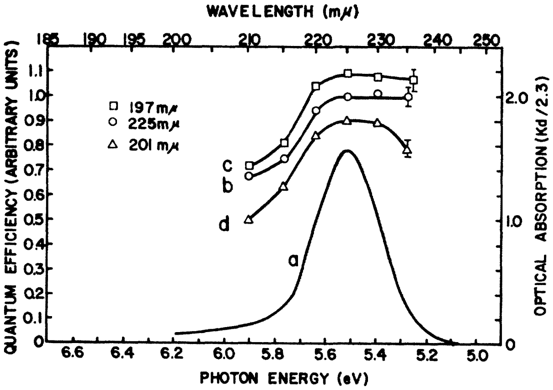

FIG. 6. a: volume optical absorption of a KBr-KH crystal at 78°K. Spectral distribution of the relative quantum efficiency: b: for destruction of *U* centers at 78°K; c and d: for growth of optical absorption at 197 and 201 mμ, respectively.

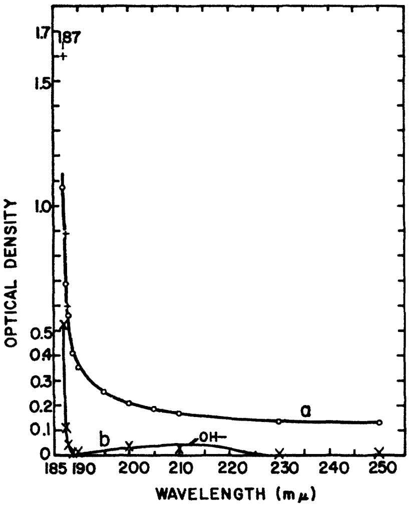

FIG. 7. a: apparent optical density due to surface reflection for a "pure" KBr crystal at 78°K; b: true volume absorption in mm^{-1} at 78°K for the same crystal. The + symbols are the sum of a and b and represent the total apparent optical density for a 2.3 mm thick crystal.

in the γ band, the 197-mμ band, and other bands in the vicinity of 200 mμ extending beyond 210 mμ. The decrease in the 197-mμ band is clearly shown in Fig. 5 which is the difference of curves c and b of Fig. 3.

The optical absorption of a KBr–KH crystal which was used for the quantum efficiency measurements is shown by curve a of Fig. 6. Curve a represents the volume absorption of the crystal; the effect of surface reflection on the measured optical density has been corrected. This correction was made by measuring the apparent optical density of "pure" KBr crystals as a function of thickness and extrapolating the results to zero thickness. The effect of multiple reflections between the faces of the crystal was also included in the calculation of the quantity $Kd/2.3$, where d is the crystal thickness, so that K is the true volume-absorption coefficient. Figure 7 shows the apparent optical density due to surface reflection and the true volume absorption of a "pure" KBr crystal. The "pure" KBr crystals had negligible optical volume absorption at wavelengths greater than 189 mμ with the exception of the small absorption band due to the accidental hydroxyl ion impurity. The maximum height of the hydroxyl ion band of the crystal from which the specimen of Fig. 6 was prepared was less than 0.1 cm^{-1}. This magnitude of hydroxyl ion band represents a hydroxyl ion concentration of less than 4×10^{15} cm^{-3}.

The quantum efficiency for the destruction of U centers was determined by irradiating the crystal with radiation of known intensity at a specified wavelength until the optical density in the vicinity of the α band had increased by approximately 0.5. The irradiation was interrupted periodically for the measurement of the optical density at 225 mμ (the maximum of the U band), at 197 mμ, and at 201 mμ. The initial change in the optical density was always a linear function of the number of absorbed quanta. After the completion of an experiment with one wavelength of irradiation, the crystal was heated to room temperature, the U band restored, and the experiment repeated with a different irradiation wavelength.

The quantum efficiency for the destruction of U centers is shown in arbitrary units as a function of wavelength and photon energy by curve b of Fig. 6. The absolute value of this quantum efficiency is 0.61 ±0.07 U centers destroyed per quantum absorbed at 225 mμ and 78°K. The quantum efficiency decreases on the high energy side of the U band and at 210 mμ is 68% of its value at 225 mμ. Curves c and d of Fig. 6 show the spectral distributions of the quantum efficiencies for the growth of optical absorption at 197 and 201 mμ. These quantum efficiencies are shown in the same arbitrary units as that for the destruction of U centers, curve b. The quantum efficiency for the growth of optical absorption at 197 mμ parallels that for the destruction of U centers to within a few percent over the wavelength region of the observations. The quantum efficiency for the growth of absorption at 201 mμ appears to decrease somewhat faster with increasing photon energy than does the corresponding quantum efficiency for growth at 197 mμ.

The spectral distributions for the quantum efficiencies for growth of optical absorption at 197 mμ were also investigated in a crystal containing 4.7×10^{17} cm^{-3} U centers. Irradiation at a given wavelength was continued until the increase in optical density in the vicinity of the α band was about 0.12. The results are shown in Fig. 8 and agree well with those of Fig. 6. Since the initial optical density of this crystal was 4.6 at 225 mμ and too large to measure accurately, the changes in the U center concentration and the quantum efficiency for the destruction of U centers could not be measured directly. If it is assumed that the ratio of the quantum efficiency for the destruction of U centers to that for the growth of the 197 mμ absorption is the same

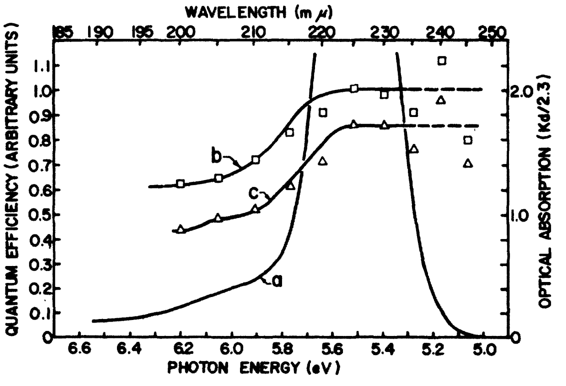

FIG. 8. a: volume optical absorption of a KBr-KH crystal at 78°K. b and c: spectral distributions of the relative quantum efficiency for growth of optical absorption at 197 and 201 mμ, respectively.

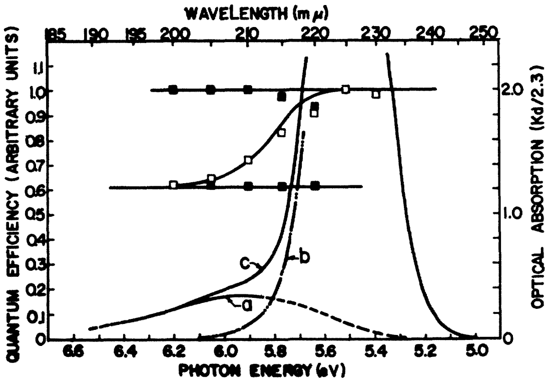

FIG. 9. Constant but unequal quantum efficiencies for the growth of 197 mμ absorption for the crystal of Fig. 8 attributed to a primary and secondary *U* band. a: The secondary band that must be assumed to obtain agreement; b: the primary band resulting from the subtraction of curve a from the measured optical absorption; c: measured optical absorption.

in this crystal and that of Fig. 6, the absolute quantum efficiency for the destruction of *U* centers in the crystal of Fig. 8 is 0.66±0.09 at 225 mμ and 78°K.

DISCUSSION

The present data show that the spectral distribution of the low temperature quantum efficiency for the conversion of *U* centers into anion vacancies differs from that of the high temperature conversion to *F* centers. At high temperatures the quantum efficiency increases with increasing photon energy; at low temperatures it decreases with increasing photon energy. In neither case is the quantum efficiency independent of wavelength as might be expected for a photochemical reaction initiated by the optical transition of a system from a ground state to a single excited state.

It is noteworthy that the *U* band is unsymmetrical; it possesses a high energy tail similar to the *K* band of the *F* center. Goto, Ishii, and Ueta have presented photoconductive evidence for the existence of two absorption bands, the U_a and the U_b bands, which are associated with excited states of the *U* center and lie on the high energy side of the *U* band.[12] Figure 9 shows the results of an attempt to explain the decrease in quantum efficiency for the growth of the 197 mμ absorption of Fig. 8 in terms of a secondary absorption band that overlaps the high-energy tail of a primary *U* band. If it is assumed that the secondary band has a constant quantum efficiency that is 61% of the quantum efficiency of the primary *U* band, the observed spectral distribution of the quantum efficiency shown by curve b of Fig. 8 can be reproduced. Curve a of Fig. 9 shows the magnitude and shape of the secondary band that must be assumed to obtain this agreement. Curve b of Fig. 9 is the primary *U* band of almost symmetrical form that results from the subtraction of the secondary band from the measured optical absorption, curve c. The absorption coefficient of the secondary band at its peak is 1/75 that of the primary band. Curve a of Fig. 9 corresponds to the U_a band of Goto *et al.*[12] The U_b band, overlapping the tail of the U_a band in KBr, appears to be included subtly in curve a of Fig. 8 in the vicinity of 190 to 195 mμ.

The bleaching of the 197 mμ band as a result of optical irradiation at 255 mμ (Fig. 5) is consistent with the thermal bleaching observations. The optical absorption by an interstitial hydride ion may result in a local state of thermal agitation of the lattice (a thermal spike). Such thermal spikes bring about the recombination of neighboring anion vacancies and interstitial hydride ions. It is noteworthy that the shape of the bands which initially bleach in this process is approximately the same as the shape of the bands which bleach thermally at 103°K.

The perturbed α bands which bleach thermally at approximately 103°K or as a result of radiation absorbed at 255 mμ in the U_1 band (Fig. 2, curve a and Fig. 5) exhibit an interesting structure. The band of Fig. 2a or Fig. 5 might be decomposed into two overlapping bands—a large band whose peak is at about 196.5 mμ and a smaller band whose peak is in the vicinity of 208 mμ. The 208-mμ band appears at a lower energy than the unperturbed α band; all other perturbed α bands in Fig. 2 appear at higher energies than the unperturbed α band.

The oscillator strengths for the α band and the perturbed α bands for the curves shown in Fig. 2 were obtained by measuring the areas of these bands and the appropriate changes in *U* band absorption at its peak. (Curves b and c of Fig. 2 were summed for this purpose.) Table I compares these data with similar data presented by Timusk and Martienssen.[8] For the unperturbed α band at 201.5 mμ, there is excellent agreement, with both workers obtaining 1.1 as the oscillator strength. The salient feature is that the present data give the same oscillator strengths for the perturbed and unperturbed α bands, whereas Timusk and Martienssen's values range from 0.5 to 1.1. It should be noted that for a small perturbation of an allowed transition one does not expect a large change in the oscillator strength.

The large disagreement for the α_1 band, which bleached at 103°K, is partially accounted for by the fact that Timusk and Martienssen did not include the 208-mμ band in their calculations. Furthermore, the belief that the 208-mμ band is part of the perturbed α band rather than a band of another origin is supported by the uniformity of oscillator strengths obtained in

TABLE I. Oscillator strengths of α bands perturbed by interstitial hydride ions.

Band position	Present data f_α	Timusk and Martienssen f_α	Designation
196.5 mμ (6.31 eV) and ≈208 mμ (5.97 eV)	1.1	0.5	α_1
200 mμ (6.20 eV)	1.1	0.8	α_2
201.5 mμ (6.15 eV)	1.1	1.1	α_3

the present work for the bands of curves a, b+c, and d of Fig. 2

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Optical Absorption and Photoconductivity in the Band Edge of β-Ga_2O_3†

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Optical absorption and photoconductivity have been observed in the ultraviolet in single crystals of nominally pure β-Ga_2O_3. At room temperature a steep absorption edge, characteristic of a band-to-band transition, is observed at 2700 Å. The edge is shifted approximately 100 Å toward shorter wavelengths when the temperature is reduced to 77°K. Photoconductivity begins coincident with the absorption edge at 77°K, but could not be detected at room temperature. A model is proposed in which the absorption arises as a result of excitation of an electron from the oxygen $2p$ band to the gallium $4s$ band. Calculations using this model and the Born-Haber cycle are in good agreement with the observed band gap of 4.7 eV. It is suggested that the much smaller band gap of β-Ga_2O_3 as compared with sapphire is due to the reduced coordination number of the ions involved in the transition.

SEVERAL important properties of the β form of Ga_2O_3 have recently been investigated in studies of the crystal structure by Geller[1] and the optical and microwave properties of Ga_2O_3:Cr by Peter and Schawlow[2] and Tippins.[3] In this paper are reported some preliminary results on the ultraviolet absorption spectrum and photoconductivity observed in the pure crystal. A simple charge-transfer model is proposed to explain the absorption process, and calculations based on this model are in good agreement with the position of the absorption edge. Several interesting features result from the relatively complicated Ga_2O_3 crystal structure not encountered for other wide-band-gap semiconductors previously studied.

The crystals used for this investigation were obtained from boules grown by Chase[4] using the Verneuil technique. The primary cleavage planes for Ga_2O_3 are (100). The crystal cleaves easily and frequently spontaneously along these planes, which makes fabrication of samples with good optical faces oriented in an arbitrary direction almost impossible. However, with sufficient care, the cleavage planes themselves provide a satisfactory surface.

Figure 1 shows the absorption edge obtained for a sample 86 μ thick. The light is incident normal to the (100) plane. These data were recorded on a Cary model 14 spectrophotometer and are not corrected for multiple internal reflections. The low-temperature data were obtained using a cold-finger-type Dewar with quartz windows. Except for the one shoulder there is very little structure. Reducing the temperature to 77°K shifts the edge approximately 100 Å to the blue but

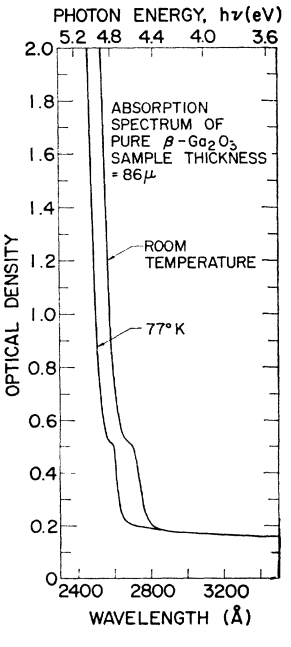

FIG. 1. Absorption edge of pure β-Ga_2O_3.

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