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Fundamental Optical Absorption in Magnesium Oxide*

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The optical absorption and reflectivity of single crystals of MgO and the optical absorption of thin films of MgO, both supported by a LiF substrate and unsupported, have been measured in the energy range from 6 ev to 13.5 ev. Absorption peaks due to impurities were observed at 6.0 ev, 6.3 ev, and 6.9 ev. The room-temperature fundamental absorption and reflectivity spectra are interpreted in terms of an exciton peak at 7.6 ev with a probable second peak at 8.8 ev. Some evidence is present for additional exciton structure on the low-energy side of the first peak. The width of the forbidden energy band in MgO is estimated to be about 8.7 ev. The effects of temperature and internal strains on the absorption spectra are discussed.

INTRODUCTION

IN addition to its importance as a highly efficient secondary electron emitter and as a high-temperature insulator, magnesium oxide is of interest because of its position as the lightest of the IIA-VIB compounds. The IIA-VIB compounds, composed of the oxides, sulphides, selenides, and tellurides of the alkaline earths are accurate divalent counterparts to the alkali halides (the IA-VIIB compounds). Not only are both families mostly of the same crystal structure (cubic NaCl) but both are made up of ions having electronic configurations similar to the rare gases. The similarity between these two groups of compounds provides an excellent opportunity for quantitative checks for theories relating to ionic solids. Comparisons between these two groups of compounds will be further discussed in future papers.

Most of the work on the optical absorption of magnesium oxide has been carried out in the impurity-sensitive region of the spectrum.[1,2] Johnson[3] has extended these optical measurements into the vacuum ultraviolet using samples of thinly cleaved crystals. He found the threshold for fundamental optical absorption to be about 7.5 ev. These measurements have been further extended by Nelson[4] who measured the reflectivity from cleaved surfaces of magnesium oxide crystals. He observed a sharp, temperature-dependent peak at 7.5 ev, which he attributed to exciton formation, and also two broad bands at 11 and 13.2 ev which were temperature independent. His estimate of the width of the forbidden band in magnesium oxide was about 10 ev.

In the work reported here, measurements of the optical reflectivity of magnesium oxide from freshly cleaved crystals and optical absorption from thin films deposited on lithium fluoride and thin unsupported films were made in the wavelength region from 2100 A to 900 A.

EXPERIMENTAL PROCEDURE

A vacuum ultraviolet spectrophotometer similar in design to those described by Parkinson and Williams[5] and by Johnson[6] was constructed for use in making the measurements reported here. The light source used was a low-voltage hydrogen arc similar to that described by Johnson.[6] The detector for the ultraviolet radiation was a sodium salicylate phosphor coated on a 1P28 photomultiplier. This was found to be the most efficient of several combinations tried. In the sample chamber, the beam of monochromatic ultraviolet radiation passed through a slot milled into a copper block which was mounted on the bottom of a liquid air Dewar. The sample was mounted on a slide which could be moved in and out of the beam through a second slot in the copper block at right angles to the first. Other slides were provided to carry filters used in making corrections for scattered light and for fluorescence of the sample. The hydrogen which filled the entire instrument at a pressure of 2 mm of Hg greatly facilitated cooling the sample by improving the thermal contact with the copper block. Thermocouple measurements indicated that the samples were cooled to −170°C. Unless otherwise indicated, all of the data included in this paper were taken with a band pass of 9 angstroms.

Both Norton[7] and Missouri[8] magnesium oxide crystals were freshly cleaved for reflectivity measurements. These crystals were thick enough (2 mm or greater) so that reflection would not occur from the back. After a sample was mounted on a metal backing, its surface was cleaned with carbon tetrachloride and alcohol. The reflectivity was measured by allowing monochromatic ultraviolet light to strike the cleaved face at an incident angle of approximately 45°. Reflected light from the crystal was directed onto the sodium salicylate phosphor which acted as a frequency converter for the RCA-1P28 photomultiplier. Since the

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* Supported in part by the Office of Naval Research.

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[6] P. D. Johnson, J. Opt. Soc. Am. **42**, 278 (1952).

[7] Supplied by the Norton Company.

[8] These crystals were grown by Harold John in our laboratory from magnesium oxide melted in a carbon arc furnace.

crystal holder could be moved into and out of the beam, the unreflected monochromatic light was also observed. The reflectivity measured was a relative quantity, since the geometric factors were not evaluated and different sections of the phosphor received the reflected and the unreflected light.

Several very thin crystals of both Norton and Missouri magnesium oxide were obtained accidentally when larger crystals were cleaved. These measured about 2 mm wide and were from 0.5 cm to 1 cm long. Their thickness ranged from about 0.17 mm to 0.63 mm. Optical absorption measurements were made both at room temperature and at −170°C.

In order to make opacity measurements of magnesium oxide in the fundamental ultraviolet region, extremely thin films of the material were necessary. The most successful films were produced on a backing of lithium fluoride. Lithium fluoride was selected as a substrate because it is transparent out to 11.5 ev. The lithium fluoride plates were cleaved to a thickness of about 2 mm, and were then given a high optical polish. This polish was necessary to avoid the development of pinholes in the film. After polishing and cleaning, a thin film of magnesium metal was evaporated on the plates. If this semitransparent film was found to be uniform and free from holes, the plate was air baked at approximately 650°C. The magnesium oxide films resulting from this process were colorless when examined by eye or under a microscope.

Considerable difficulty was experienced in making unbacked magnesium oxide films without holes or cracks. The most successful method for making these films is described as follows: one part of collodion was diluted with three parts of amyl acetete and a few drops of this mixture were placed on distilled water and allowed to harden. The collodion film was then mounted in a vacuum bell jar and magnesium metal evaporated on it. After the magnesium-covered collodion was removed from its mount, it was placed on a nickel screen (collodion face up) and heated in a dry hydrogen atmosphere at 600°C for 5 minutes. This procedure removed the very thin layer of collodion and left the magnesium film intact and partially free of the nickel screen. The magnesium film was then heated in air for 10 minutes at 650°C. Later, when the resulting magnesium oxide film had cooled in a desiccator, it was carefully removed from the nickel screen and examined under a microscope for holes and cracks using reflected light. The unbacked films measured were clear and brittle.

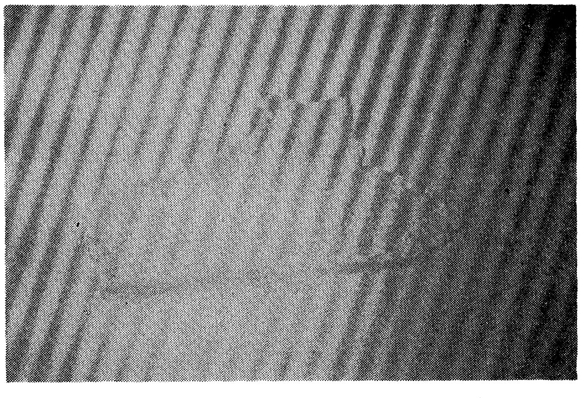

FIG. 1. Thin, unsupported film of MgO, No. 29, photographed between two optical flats using 5839-A light. Longest dimension of film is about 1.5 cm. Thickness of film calculated from shift of the interference fringes and using 1.7 for the index of refraction is 2×10^{-5} cm.

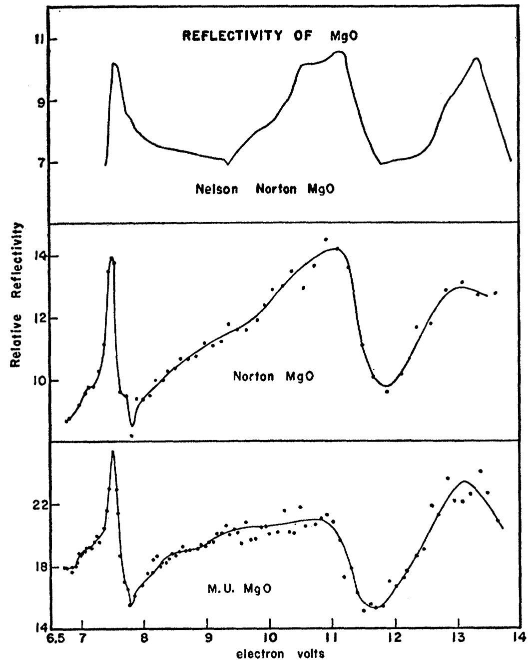

FIG. 2. Relative reflectivity at room temperature for Norton and Missouri single crystals of MgO. At top are shown Nelson's results for a Norton crystal at room temperature replotted on a linear energy scale.

By observing the interference fringes of the film between two quartz optical flats, the thickness of several unbacked films was measured. Most of the films studied were of the order of 2000 A thick. A photograph of film No. 29 is shown in Fig. 1. Weight measurements confirm that the shift is less than one complete fringe. Using an index of refraction for magnesium oxide of 1.7, the thickness of this sample was determined to be approximately 2×10^{-5} cm.

EXPERIMENTAL RESULTS

The results of the reflectivity measurements are shown in Fig. 2. Also shown in this figure are the room-temperature results obtained by Nelson[4] on Norton crystals, replotted on a linear energy scale. Although the data shown in Fig. 2 was taken early during the investigation, and there was considerable scatter in the experimental points, it will be observed that there is general agreement on the principal features of these

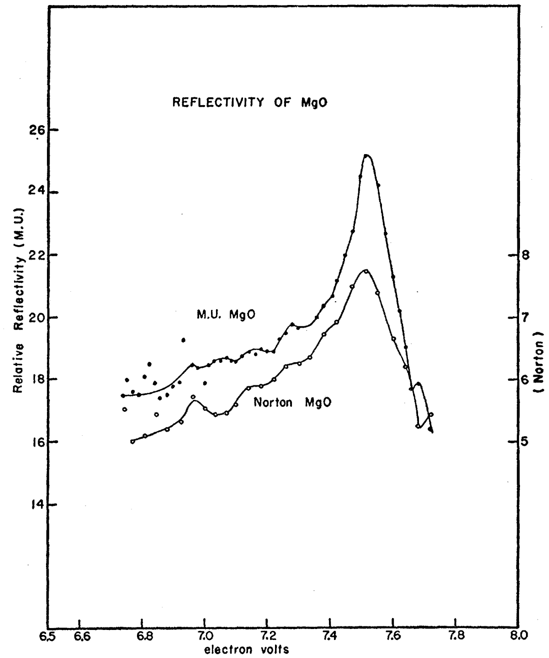

FIG. 3. Relative reflectivity at room temperature for Missouri and Norton single crystals of MgO showing minor structure on low-energy side of first exciton peak.

curves. The sharp peak at 7.55 ev is believed to be due to the formation of excitons. The two very broad bands which peak at approximately 11 ev and 13.2 ev are believed to be associated with the band-to-band transitions.

Important differences will be observed in the spectra reported here as compared with Nelson's results in the region from 7.5 ev to 9.5 ev. First, the reflectivity is observed to drop sharply on the high-energy side of the 7.5-ev peak with a distinct minimum at about 7.7 ev. Second, the reflectivity increases slowly over a broad region to the right of this minimum. The significance of these features will be discussed in the last section. It should be pointed out that this region of principal disagreement with Nelson's results is a region of rapidly changing light intensity in the hydrogen arc spectra.

Very careful measurements of the reflectivity on the low-energy side of the 7.55-ev peak gave some indication of structure. Data taken on a Norton and a Missouri crystal are shown in Fig. 3. For these measurements, the band pass of the monochromator was reduced to 5 angstroms. Although the observed peaks are not pronounced and consequently must be regarded as tentative, they were observed in several samples each of Norton and Missouri crystals. The positions of these peaks appear to be at 7.4 ev, 7.28 ev, 7.16 ev, and 6.96 ev. In most curves, a weak peak at 7.7 ev was also observed.

The optical absorption in thin crystals of both Norton and Missouri crystals is shown in Fig. 4. In the Norton crystal, this absorption was measured at both room temperature and at −170°C. The low-temperature absorption was not made for the Missouri crystals because of difficulties brought about by the fluorescence of these crystals. In all crystals measured, a strong absorption set in at about 7.2 ev and extended out to at least 13 ev. The absorption was greater than 500 cm^{-1} at 7.5 ev in every crystal studied. For the Norton crystals, this fundamental absorption edge shifted somewhat toward higher photon energy at the low temperature.

Because the absorption at the lower energies is strongly dependent upon the sample being studied, this absorption should be attributed to impurities or lack of stoichiometry in the crystals. Some sharpening was observed for these absorption bands at the low temperature. In the spectrum for the Norton crystals, three impurity bands may be seen at approximately 6.0 ev, 6.3 ev, and 6.9 ev.

Although the Missouri crystals measured were considerably clearer in this region, a slight peak is seen to occur at about 6 ev. Measurements were difficult on the Missouri crystals because of the strong fluorescence. Corrections for this fluorescence were made by use of selective filters. The absence of this strong fluorescence in the Norton crystals, which have a somewhat larger impurity content, should probably be attributed to the quenching of the fluorescence by the additional trapping states.

Measurements of the opacity of four typical films made by oxidizing magnesium evaporated on lithium

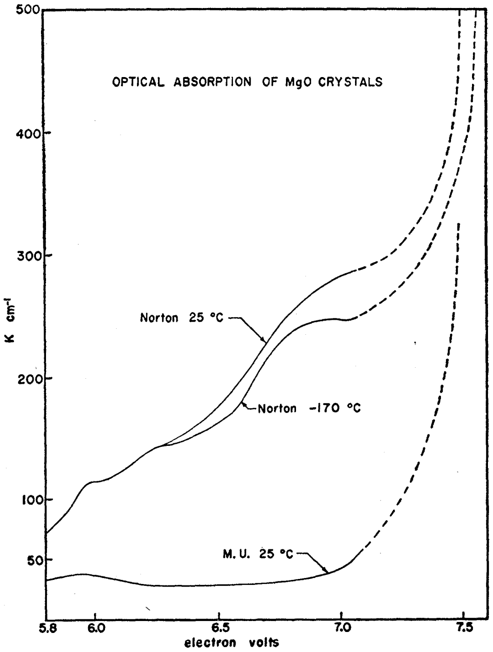

FIG. 4. Optical absorption in thin single crystals of MgO. The Missouri crystal was 0.28 mm thick and the Norton crystal was 0.17 mm thick.

fluoride are shown plotted on a logarithmic scale in Fig. 5. These curves were obtained at room temperature. No correction was made for reflectivity. However, it is doubtful if such a correction would have changed the general shape of these curves. Since the optical absorption is linearly related to the logarithm of the opacity, these plots may be considered to be the same as optical absorption curves multiplied by the thickness of the film. The thickness of the 2500-angstrom film was obtained by measuring the shift of interference fringes produced between the sample and an optical flat, using several wavelengths of light. The thicknesses indicated for the thinner films were inferred by assuming that the absorption of the first peak was proportional to this thickness.

The curves in Fig. 5 show a sharp rise in absorption starting at 7.5 ev, and reaching a peak at 7.9 ev. A second peak may be seen at about 8.8 ev. Another broad maximum is observed starting at about 9.5 and reaching a maximum between 10.5 and 11 ev. Notice that the upper curve in Fig. 5 shows the 10.5-ev peak lower in relation to the 7.9-ev rise. This type of curve was observed only on one film and should probably be attributed to an inadequate correction for scattered light. This sample was transmitting less than 1% of the ultraviolet light while passing most of the scattered white light.

Opacity measurements were also made on these films at liquid air temperature. At low temperature, no sharpening of the peaks was observed, but there was observed a slight shift to higher energies. Data taken for the 650-A film are shown in Fig. 6. Similar data were observed for other films. In one case, measurements were made at 150°C, room temperature, and -170°C. The temperature dependence of the position of the peak was found to be approximately -5×10^{-4} ev/°K.

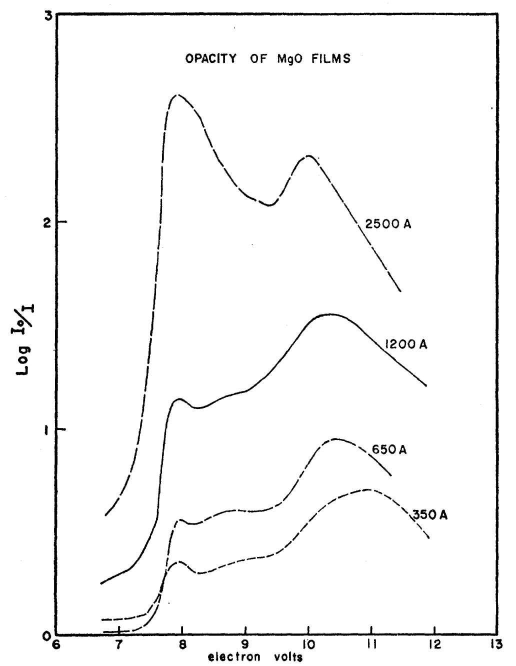

FIG. 5. Opacity of thin films of MgO on a LiF substrate measured at room temperature. The thickness of the 2500-A film was measured from the shift of interference fringes at edge of film. The indicated thicknesses for the other films were calculated on the assumption that the logarithm of the opacity at 7.9 ev was proportional to the thickness.

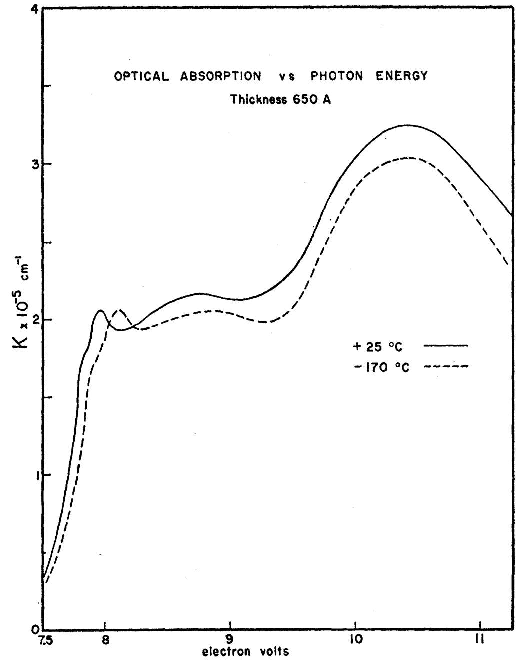

FIG. 6. Effect of temperature on optical absorption in thin film of MgO on LiF substrate.

Opacity measurements on the thin unbacked films were made both at room temperature and at -170°C. At the lower temperature, a slight sharpening and shift to higher energies was observed for the 7.8-ev peak, similar to the case of the backed films. The opacity of three typical unbacked films is shown in Fig. 7 for measurements made at -170°C. The exciton peak is observed at approximately 7.85 ev with a second peak at 8.8 ev. A broad peak is observed at about 11 ev, and in the thinnest sample, a second broad maximum occurs at about 13.2 ev. Only in two samples was this 13.2-ev peak observed. Since lithium fluoride does not transmit ultraviolet beyond 11.5 ev, the 13.2-ev peak was not observed in the case of the backed films.

The lack of sharpness for the exciton peak and the absence of any significant narrowing of this peak at low temperatures is probably due to the presence of excessive strains in the thin films. Attempts to anneal the films formed on the lithium fluoride backing were unsuccessful, probably because of the difference in thermal expansion of the two materials. Three of the unbacked films were annealed at 1000°C for three hours. However, only one of these films was suitable for measurements after this process. The other films

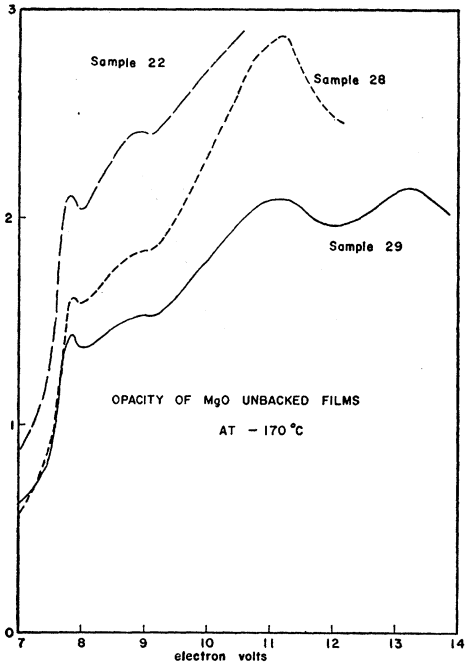

FIG. 7. Opacity of thin, unsupported films of MgO measured at −170°C. Thickness of film No. 29 was 2×10^{-5} cm as determined by shift of interference fringes shown in Fig. 1.

developed holes during the annealing or else cracked during mounting. Measurements at −170°C on the successful film are shown in Fig. 8. The exciton peak for this film before annealing was not as sharp as was generally observed. However, it occurred between 7.8 ev and 7.9 ev. Nevertheless, the annealed film showed a sharpening of this peak as well as a shift to 7.65 ev. This peak was also less sharp at room temperature. A rather unexpected effect of the annealing was the increase in opacity of the annealed film. Also at both room temperature and low temperature, the 13.2-ev peak appears either to have disappeared or to have shifted to lower energy. The reasons for this effect are not at present understood.

DISCUSSION

Because of its high absorption constant, the optical absorption in magnesium oxide above about 7.5 ev may be safely attributed to fundamental absorption. However, it is difficult to separate the absorption associated with excitons from that due to direct band-to-band transitions and to analyze the details of the spectra for these two processes. The changes in these spectra brought about by the presence of strains and gross imperfections in the crystal still further complicate the situation.

The first major peak in the reflectivity spectrum is undoubtedly an exciton peak. This follows from its sharpness and the fact that, as observed by Nelson,[4] it becomes sharper at low temperatures.

The shape of the reflectivity spectrum in this region is determined largely by the real part of the index of refraction. This may be seen from considerations of the Fresnel equation for reflectivity,

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2},$$

where n and k are the real and imaginary parts of the index of refraction, respectively, and the fact that the reflectivity in this region is, in general, less than about 25%. In the region of a sharp optical absorption, the real part of the index of refraction is characterized by an anomalous dispersion curve. The pronounced minimum in the reflectivity data shown at 7.7 ev in Fig. 2 is strongly suggestive of such a behavior. Consequently, the position of the exciton absorption peak should occur in the region of the sharpest falloff of the reflectivity on the high-energy side of the peak or at about 7.6 ev at room temperature.

The position of the principal exciton peak in the room-temperature absorption data varies from about 7.9 ev for the films supported on a backing of lithium fluoride to about 7.65 ev for the annealed, unbacked films. This variation in the position of the exciton peak should probably be attributed to internal strains in the samples. In the lithium fluoride backed samples, these strains are probably due primarily to the difference in thermal expansion of the two materials. In the case of the unbacked films before annealing, these strains are

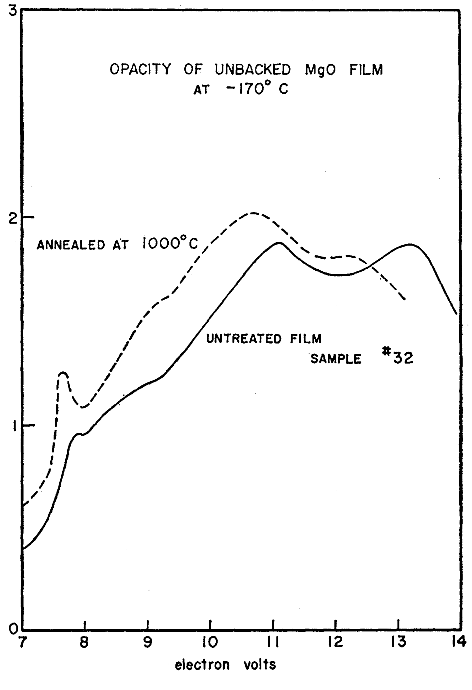

FIG. 8. Effect of annealing for 3 hours at 1000°C on opacity of thin unsupported film of MgO. Measurements were made at −170°C.

probably due to gross deformation brought about in the growth process. It will be noted that the shift in the exciton peak due to strains is opposite to that produced by increasing the temperature. The reasons for this are not yet fully understood. On comparing the region of sharpest falloff in the reflectivity data with the position of the exciton peak in the annealed, unbacked film, the most probable value for the first exciton peak in an unstrained crystal at room temperature appears to be about 7.6 ev.

A second peak in the optical absorption data may be seen at about 8.8 ev. Although this peak is rather broad, it is believed that it also should be attributed to the formation of excitons. Probably the best evidence for this comes from a study of the photoelectric emission from magnesium oxide.[9] Exciton-induced photoelectric emission results from a two-step process in which the light quantum first produces an exciton which in turn gives up its energy in an Auger process to a donor electron. Changes in the stoichiometric composition of magnesium oxide brought about by heating the sample in an atmosphere of oxygen were observed to alter the photoelectric yield in the region of 8.8 ev. On the other hand the yield above about 10 ev was not affected by this process, thus indicating direct transitions from the filled band. Since the yield at 8.8 ev was too high (greater than 10^{-2} electrons/quantum) for direct transitions from the donors, this may be taken as positive evidence for the production of excitons at this energy.

A qualitative similarity may be observed between the absorption spectra for magnesium oxide observed here and the spectra for barium oxide obtained by Zollweg.[10] The absorption spectra due to excitons which one would expect from materials such as these have been examined by Overhauser.[11] His conclusion is that ionic crystals having a sodium chloride structure will in general have 5 lines in the exciton multiplet. In materials in which the spin-orbit interaction is weak compared with the other interactions involved, two of these lines will be strong and three will be weak. It is therefore tempting to identify the two strong peaks observed at 7.6 ev and 8.8 ev with those predicted by Overhauser and the minor structure observed on the low-energy side of the first peak in the reflectivity shown in Fig. 3 with the weak transitions. Although this minor structure was not observed in the optical absorption measurements on the thin films, it must be remembered that these polycrystalline films are far less perfect in structure than the single crystal used for the reflectivity data. More work using more refined techniques should be carried out to resolve these possibilities.

Estimates have been made of the width of the forbidden energy band in magnesium oxide, but in general the evidence has been very meager. Using soft x-ray emission measurements, O'Bryan and Skinner[12] have estimated the band gap to be about 10 ev. Watanabe[13] studied the loss in energy of high-velocity electrons scattered by thin foils of magnesium oxide. He observed peaks in the absorption spectrum of the electrons at 4.5 ev, 5.5 ev, 11.4 ev, and 25 ev. He interpreted the 11.4-ev peak to be due to band-to-band transitions. However, it is well to note that in his data there is no peak that corresponds to the 7.6-ev exciton absorption, which raises a question regarding the interpretation of his data. Nelson[4] estimated the forbidden band gap to be approximately 10 ev on the basis of his reflectivity data. Although this value is plausible for his data, the reflectivity data presented here are quite different in the region from 8 to 10 ev.

If the 8.8-ev peak is due to an exciton transition as is suggested here, then it probably covers the threshold for the band-to-band transitions. Extrapolation of the absorption underlying this peak seems to lead to a value somewhere between 8 and 9 ev. We estimate the most probable value for the threshold of the band-to-band transitions to be about 8.7 ev.

The absorption spectra for the band to band transitions show two broad peaks near 11 ev and 13 ev in both the spectra of the reflectivity and the opacity of the unannealed unbacked films. Annealing these films brings about a change in this spectrum that is difficult to understand. Although these spectra are probably related to the density of states in the filled band of magnesium oxide, there is little more that can be stated at the present time.

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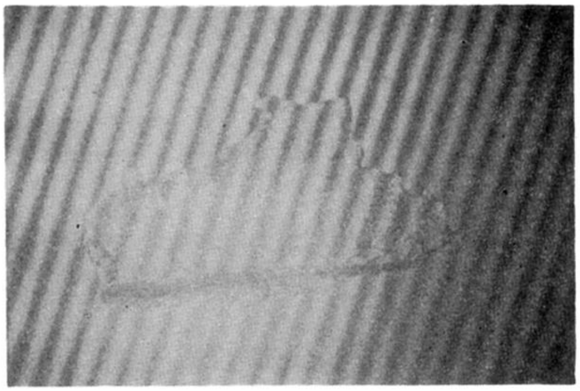

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