

differs from  $(1+S)^{-\frac{1}{2}}$  in a term of a third order in  $S$ . It is readily seen that the Löwdin orthonormal functions extremize the magnitude of

$$\sum_k (u_k, v_k^*).$$

By proceeding as above, we are led to the equation

$$(u_s^*, v_t) \sum_k (u_k, v_k^*) + \lambda_{st} = 0, \quad (24)$$

and hence to

$$(u_s^*, v_t) \sum_k (u_k, v_k^*) = (u_t, v_s^*) \sum_k (u_k^*, v_k). \quad (25)$$

Since  $\lambda_{ss}$  is real,<sup>3</sup> we have

$$(u_s^*, v_s) \sum_k (u_k, v_k^*) = \text{real quantity}, \quad (26)$$

and hence conclude that all  $(u_s^*, v_s)$  have the same phase angle. Therefore the sum

$$\sum_k (u_k, v_k^*)$$

may be made real by the same change of phase in all the  $v$ 's, and hence Eq. (25) implies that  $(u_s^*, v_t) = (u_t, v_s^*)$ , i.e.,  $X = X^\dagger$ , and therefore  $X = (1+S)^{\frac{1}{2}}$  by Eq. (14).

## Storage of Energy in Beryllium Oxide\*

H. O. ALBRECHT AND C. E. MANDEVILLE

*Bartol Research Foundation of the Franklin Institute, Swarthmore, Pennsylvania*

(Received January 3, 1955; revised manuscript received November 21, 1955)

The photostimulated ultraviolet emission of x-ray excited BeO has been measured as a function of the wavelength of the incident light. A maximum of emission occurs for a stimulating wavelength of  $\sim 4100$  Å. Experiments are described which are interpreted as showing the presence of doubly occupied traps in BeO which are analogous to the  $F$ -centers of the alkali halides. Some discussion concerning energy storage in NaCl(Ag) is included.

### INTRODUCTION

IN previous notes,<sup>1,2</sup> the writers have described some of the characteristics of the luminescent properties of beryllium oxide. The earlier measurements as well as those of the present paper were carried out at room temperature,  $\sim 22^\circ\text{C}$ . It has been shown<sup>1,2</sup> that both ultraviolet and visible fluorescence and phosphorescence are observable when BeO is irradiated by high-energy particles. In addition, some of the electrons of the solid which are removed from the filled band by action of the primary excitant are subsequently trapped for periods of great duration so that energy is stored in the phosphor. One means of removal of the electrons from the deep traps is the method of photostimulation whereby incident photons eject trapped electrons which enter the conduction band, whence they return to the filled band by way of luminescence centers.<sup>3</sup> It is in the course of proceeding through the luminescence centers that luminous emission occurs. In the case of BeO, the emission band extends from a wavelength of  $\sim 2000$  Å to more than 4000 Å. A part of the ultraviolet portion of this spectrum is readily detectable in photosensitive Geiger counters which can be specially selected to respond only in the vicinity of 2600 Å and not at all to

longer wavelengths, so that the photostimulating radiation is not detected. Thus, the observation of the photostimulated ultraviolet emission was simultaneous with application of the stimulating light.

The method has a particular advantage over absorption measurements in this case in that suitable single crystals of BeO are not as yet obtainable for the latter purpose.

### PROCEDURE

To observe the photostimulated emission of BeO, a slurry of powdered material was painted upon a platinum disk and x-rayed in darkness. After having been retained in darkness for a sufficient time to allow the afterglow to become negligible, the disk was placed in an optical system which has been previously described.<sup>4</sup> The ultraviolet emission was measured as a function of the wavelength of the photostimulating light as shown in Fig. 1 where a maximum is seen to occur near 4100 Å. This curve is to be compared with a similar one for NaCl(Ag) which is also presented in Fig. 1. To obtain the curve for silver-activated NaCl, a polycrystalline melt of NaCl(Ag) was irradiated by the beta rays of RaE in an exposure of 12 millicurie-hours. The irradiated material was then allowed to remain in darkness for a period of sixteen months at  $22^\circ\text{C}$  after which time the curve of Fig. 1 was observed. This plot of the photostimulated emission of NaCl(Ag) is identical with absorption curves which are noted

\* Assisted by the joint program of the Office of Naval Research and the U. S. Atomic Energy Commission.

<sup>1</sup> C. E. Mandeville and H. O. Albrecht, *Phys. Rev.* **94**, 494 (1954).

<sup>2</sup> H. O. Albrecht and C. E. Mandeville, *Phys. Rev.* **94**, 776 (1954).

<sup>3</sup> The activating elements in the various samples of BeO used are yet unknown, although spectrographic analyses were performed.

<sup>4</sup> C. E. Mandeville and H. O. Albrecht, *Phys. Rev.* **97**, 347 (1955).

when excited crystals of pure NaCl are irradiated in the *F*-band. Thus, the photostimulated emission results from the destruction of *F*-centers by the incident light.<sup>5</sup>

On considering the similarity of the two curves of Fig. 1, it was concluded that the same mechanism might be operative in the case of both solids; that is, just as the curve of Fig. 1 relating to NaCl(Ag) arises from the release of electrons from *F*-centers, so might the data for BeO result from a similar process. An "*F*-center" would appear in BeO when *two* electrons are trapped at a vacant lattice site normally occupied by an oxygen ion.

To ascertain whether the emission curve for BeO in Fig. 1 resulted from the destruction of *F*-centers, samples of BeO were processed in a cycle of heat treatments in a quartz tube. The heat was supplied by a high-frequency induction furnace. Temperatures were determined by an optical pyrometer. The temperatures were relative, because black-body conditions did not prevail. After each phase of the cycle, the BeO was allowed to cool, removed from the furnace, x-rayed, and subsequently photostimulated under a set of standard conditions.

The first heating was *in vacuo*, the second in oxygen at 1 atmos, etc. Heating periods of 5 minutes to three hours were employed without marked variation in the

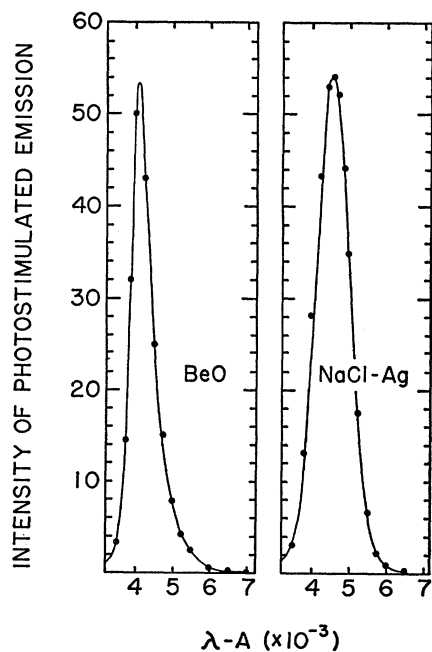


FIG. 1. Photostimulated emission of x-rayed BeO and beta-irradiated NaCl(Ag) as a function of the wavelength of the incident light. All operations were carried out at  $\sim 22^\circ\text{C}$ . The sample of NaCl(Ag) was held at this temperature for sixteen months in darkness prior to photostimulation.

<sup>5</sup> It is estimated that when three grams of NaCl(Ag) were excited and stored in darkness for 16 months as described above, about one billion ultraviolet photons per second could be drawn from the material by photostimulation with a conventional 3-volt flashlight.

TABLE I. Heat treatment of beryllium oxide.

<i>T</i> ( $^\circ\text{C}$ )	Time (min)	Gas	Pressure (atmos)	Photostimulated intensity (counts per min)
950	60	O <sub>2</sub>	1	7200
950	60	Vac.		6200
1150	60	Vac.		26 400
950	60	O <sub>2</sub>	1	12 100
1150	60	Vac.		39 200
950	60	Vac.		8400
1150	60	Vac.		37 200
950	60	Vac.		10 000
1150	60	Vac.		35 500
950	60	Vac.		9200
1150	60	Vac.		45 800
1150	60	N <sub>2</sub>	1	38 100
1150	60	O <sub>2</sub>	1	2700
1150	60	Vac.		37 000
1150	5	O <sub>2</sub>	1	8100
1150	5	Vac.		26 400
1150	5	O <sub>2</sub>	1	7200
1150	5	Vac.		21 000
1150	5	O <sub>2</sub>	1	5100
1150	5	O <sub>2</sub>	1	2800
950	60	Vac.		180
1150	5	Vac.		13 200
950	5	Vac.		2400
1150	60	Vac.		45 600
20	150	O <sub>2</sub>	133	44 500
950	120	Vac.		7100
1150	120	Vac.		42 000
760	120	Vac.		730
760	30	H <sub>2</sub>	1	2600
950	120	H <sub>2</sub>	1	7800
950	195	H <sub>2</sub>	1	7600
950	5	O <sub>2</sub>	1	9600
950	10	O <sub>2</sub>	1	9200
950	60	Vac.		8300
1050	60	Vac.		15 200
1050	60	Vac.		11 200
1150	60	Vac.		24 800

results. A several-fold diminution of the peak photostimulable intensity resulted from the oxygen treatment. The intensity of the emission could be restored by a further heating *in vacuo*. The largest effects were, of course, encountered at the highest temperature employed,  $\sim 1150^\circ\text{C}$ . A long series of such measurements was performed with many samples of BeO. The extent of energy storage in a given quantity of BeO could be predicted for a particular x-ray dose, depending upon whether the sample had been previously heated in oxygen or *in vacuo*. The data of a typical set of successive measurements on a particular specimen of BeO at a variety of temperatures are shown in Table I. This sample of BeO, from the Fisher Scientific Company, was found to be more active than spectroscopically pure materials obtained from Johnson, Matthey, and Company, Ltd.

It will be noted from the table that at a lower temperature, e.g.,  $950^\circ\text{C}$ , the difference between heating *in vacuo* or in oxygen is negligible. This result can be explained by the fact that the equilibrium pressure for the dissociation of BeO at  $950^\circ\text{C}$  is less than the partial pressure of oxygen in the diffusion pump vacuum used. Heating in hydrogen and nitrogen gave results similar to treatment *in vacuo*, because the partial pressure of

oxygen was again low. Thus, heating in oxygen could be interpreted as resulting in an occlusion of oxygen to fill negative ion vacancies whereas heating *in vacuo* caused an evolution of oxygen from the powdered BeO to produce vacancies. It was found that the above-described sequence of results could be observed reproducibly.<sup>6</sup>

#### DISCUSSION

At the starting point of any investigation of a particular sample of BeO, it is evident that numerous Schottky vacancies must be present; that is, positive- and negative-ion vacancies are distributed throughout the material in equal numbers. The disturbance associated with the departure of oxygen atoms from the lattice could easily result in the appearance of two electrons in the conduction band from which they might proceed to oxygen ion vacancies. It is not probable that the electrons fill the vacancies in pairs, because since Schottky vacancies are present in the first instance, there are many more negative-ion vacancies than there are electrons to fill them. Consequently, there can result a distribution such that, for the most part, single electrons are trapped in negative-ion vacancies.

Upon exposure to x-rays, an additional electron may sometimes be added to a vacancy already occupied by one electron. It is one of these two electrons which may be removed from the negative-ion vacancy by photostimulation at the wavelengths employed in these measurements. After return to the conduction band, the electron which has been freed by photostimulation may proceed to the filled band by way of a luminescence center so that light emission occurs. Figure 1 may then be interpreted as showing that the most probable wavelength for removal of an electron from a doubly occupied trapping center in BeO is  $\sim 4100$  Å.

Some conclusions of a qualitative nature can be drawn concerning the energy levels of a doubly occupied trapping center in BeO. The widths of the emission curves of Fig. 1 are described by the expression<sup>7</sup>

$$\Delta\lambda \propto \lambda_m^{\frac{3}{2}}(kT/hc)^{\frac{1}{2}},$$

where  $\lambda_m$  is the wavelength of the photostimulating

<sup>6</sup> It might be argued that the luminescence efficiency of BeO could be affected by the heat treatment. For example, an evolution of the activating elements might occur at temperatures as high as 1150°C. This possibility seems unlikely, because the intensity of the photostimulated emission did not decrease continuously with heating but oscillated in a manner dependent upon the atmosphere in which heating took place. To investigate further this point, the alpha-particle excited fluorescence of the treated sample of BeO was measured both after heating in oxygen and after heating *in vacuo*. In either case, the fluorescent emission was the same, showing the luminescence efficiency to be undisturbed by the application of heat.

<sup>7</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1948), second edition, p. 116.

light for maximum emission. Thus, for a constant temperature, and any one given substance, the band width should increase as  $\lambda_m^{\frac{3}{2}}$ . If the peak values of emission are taken to be, respectively,

$$[\lambda_m]_{\text{BeO}} = 4100 \text{ Å and } [\lambda_m]_{\text{NaCl(Ag)}} = 4750 \text{ Å,}$$

the width of the curve for NaCl(Ag) calculated from the width of the curve for BeO is not nearly so broad as is observed. This result indicates the probability that the potential functions of the ground state and first excited state of the doubly occupied trapping center of BeO are markedly different in shape from those of an *F*-center of NaCl if plotted against a configurational coordinate.

An attempt has been made to compare the energy levels of a trapping center formed by occupation of a negative-ion vacancy in BeO by one or two electrons with the first excited states of He II or He I available from spectroscopic data.<sup>8</sup> The first excited states of He II involve the optically allowed transitions  ${}^2P_{\frac{3}{2}} \rightarrow {}^2S_{\frac{1}{2}}$ . If the transition energy is divided by the square of the dielectric constant of BeO, an energy of 4.7-ev results. For He I, the energy of the transition  ${}^3P_1 \rightarrow {}^1S_0$  is calculated analogously to be 2.4 ev. These values are to be compared with the energy difference observed in these measurements for the ground state and first excited state of the trapping center in BeO. The peak of Fig. 1 at  $\sim 4100$  Å corresponds to an energy of  $\sim 3.0$  ev, favoring somewhat the interpretation that the oxygen ion vacancy is doubly occupied.

Since aluminum is frequently found as an impurity in beryllium compounds, and since the introduction of  $\text{Al}_2\text{O}_3$  into the lattice of BeO would result in formation of positive-ion vacancies, experiments were performed to ascertain whether the energy storage might relate to trapping of positive holes at these positive-ion vacancies. This possibility seemed unlikely, because the behavior of the compound during the heat treatments could best be explained by escape of the gaseous component, thus producing negative-ion vacancies. However, 1 percent by weight of powdered  $\text{Al}_2\text{O}_3$  was added to BeO, and the mixture was heated to 1350°C for several hours. Under these circumstances, diffusion of alumina into the lattice of BeO could have occurred. In any event, no increase in energy storage capacity was observed.

#### ACKNOWLEDGMENTS

The writers wish to express appreciation for relevant discussions with Dr. J. F. Marshall and Dr. J. H. Bodine, both of Bartol. The kind interest of Dr. W. F. G. Swann is also acknowledged.

<sup>8</sup> R. F. Bacher and S. A. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932), first edition, pp. 220-223.