

each specific case. However, our approach here is rather a suggestive one, indicating the possibil-

ity of the existence of bound states and the form of the corresponding energies of excitation.

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## $F^+ \leftrightarrow F$ Center Conversions in Magnesium Oxide<sup>†</sup>

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$F$  centers are observed to be converted to  $F^+$  centers by light in the  $F$  band. Heating the crystals results in the reverse of this process, accompanied by  $F$ -band luminescence. Thermal-luminescence measurements reveal several glow peaks, the most prominent being at 500 °K. We estimate the trap depth for this glow peak to be about 1.1 eV. This trap was identified by a combined thermoluminescence-electron-spin-resonance study to be  $Fe^{2+}$ , the process being  $F + Fe^{2+} \leftrightarrow F^+ + Fe^{1+}$ .

### I. INTRODUCTION

The  $F^+$  and  $F$  centers in MgO (anion vacancies containing one and two electrons, respectively) have been the subject of several recent investigations. The  $F^+$  center was first identified by Wertz *et al.*<sup>1</sup> from its electron spin resonance (ESR) spectrum in neutron irradiated MgO. An absorption band at 5.0 eV was identified as the  $F^+$  band by correlating its magnitude with the intensity of the ESR spectrum<sup>2,3</sup> and its position with the paramagnetic Faraday-rotation pattern.<sup>4</sup>  $F$  centers have been produced in MgO<sup>5</sup> using additive-coloring techniques<sup>6</sup> similar to those which had previously been used to produce  $F$  centers in CaO<sup>7</sup> and SrO.<sup>8</sup> The resulting optical absorption band was very similar to the  $F^+$  band which led to some initial un-

certainly regarding the correctness of the identifications.<sup>9</sup> However, the discovery of an  $F \rightarrow F^+$  photoconversion process made it possible to clearly distinguish the differences in the two absorption bands and to verify the original identifications.<sup>10</sup> In this last paper, the luminescence bands associated with the  $F^+$  and  $F$  centers were observed to peak at 3.1 and 2.4 eV, respectively.

The  $F \rightarrow F^+$  photoconversion process in MgO may be described as follows: Most of the anion vacancies in an additively colored crystal in thermal equilibrium will be in the  $F$  state. Irradiation with light in the  $F$  band results in electrons being released from the  $F$  centers to the conduction band from which some of them will become trapped in impurity centers. This leaves the vacancies in the  $F^+$  state, as can be verified by the appearance or

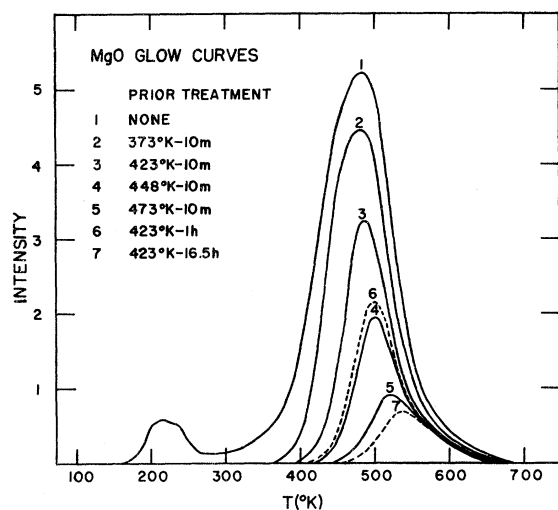


FIG. 1. Thermoluminescence from an additively colored single crystal of MgO which was cooled to 77 °K and photoconverted to the  $F^+$  state. Curve 1 shows the entire thermoluminescence spectrum. Curves 2-7 show the results of preheating to the individual temperatures for the indicated times. A linear heating rate of 0.5 °K/sec was used for all glow-curve measurements. All curves originated at 77 °K.

growth of the  $F^+$  ESR spectrum. Heating the crystals results in the release of these trapped electrons and their recombination with  $F^+$  centers to reform  $F$  centers. This process is accompanied by the emission of  $F$ -band luminescence. In this paper it will be shown that the principal traps involved in this process for all of the crystals examined to date are  $Fe^{2+}$  impurities. Using thermoluminescence techniques, the trap depth for the trapped electrons in the  $Fe^{1+}$  ions is estimated to be about 1.1 eV.

## II. EXPERIMENTAL DETAILS

The single crystals of MgO used in this investigation were produced by W. & C. Spicer, Ltd., St. Mary's Winchcombe, England. Spectroscopic analysis of these crystals detected an impurity content of about 10 ppm for Ca and Al and 1 ppm for Si, Fe, and Cu. Details of the procedures used for additively coloring these crystals and making optical absorption and luminescence measurements have been given in previous publications.<sup>8,10</sup> During glow-curve measurements the monochromator was set at the peak of the  $F$  luminescence band (wavelength of 516 nm) with the slits opened wide (bandpass of 40 nm). Although only the  $F$  luminescence band was seen in the spectra for any of the glow peaks, this procedure helps to ensure that only electron traps are being observed. A linear heating rate of 0.5 °K/sec was used for all measurements reported here.

## III. THERMOLUMINESCENCE

Curve 1 in Fig. 1 shows the thermoluminescence curve observed from an additively colored crystal. This crystal was initially colored to a density of  $5 \times 10^{17}$   $F$  centers per  $cm^3$ . After mounting in the luminescence Dewar and cooling to 77 °K, the crystal was irradiated with light in the  $F$  band for a period of time sufficient to saturate the photoconversion. The thermoluminescence curve shows two small unresolved peaks below room temperature and a large peak around 500 °K. Similar data were obtained for several other crystals. The intensities and positions of the small peaks below room temperature varied from crystal to crystal. However, all of the crystals examined showed the large peak at 500 °K.

It was possible to isolate the large glow peak at 500 °K by preheating the crystals to selected temperatures. Curve 2 in Fig. 1 was obtained by again photoconverting the crystal to the  $F^+$  state at 77 °K and then heating it to 373 °K for 10 min. Curves 3, 4, and 5 were similarly obtained by preheating to 423, 448, and 473 °K for 10 min, respectively. Curves 6 and 7 were obtained by preheating the crystal to 423 °K for 1 h and 16.5 h, respectively. All the glow curves originated at 77 °K.

A comparison of curves 4 and 5 with curves 6 and 7 in Fig. 1 shows that preheating to successively higher temperatures and preheating at the same temperature for successively longer periods of time, produce similar effects on the 500 °K emission peaks. This is taken to indicate that the 500 °K peak in curves 3-7 is essentially clean and is due to the untrapping of a single level. On the other hand, close inspection of curves 1 and 2 reveals a slight shoulder on the low-temperature side of the 500 °K peak which indicated the probable presence of a weak peak at about 450 °K.

The thermal activation energy for the trap responsible for the 500 °K peak was determined using the initial rise method of Garlick and Gibson.<sup>11</sup> The value obtained using curves 3-7 was  $E = 1.15 \pm 0.02$  eV. Curve 2 gave a value of 0.94 eV which is further evidence that the peak in curves 1 and 2 is composite.

## IV. IDENTIFICATION OF TRAPS

A combined thermoluminescence-ESR study was undertaken in an effort to determine the identity of the traps responsible for the various glow peaks. In freshly cleaved crystals, ESR spectra were observed from  $Mn^{2+}$ ,  $V^{2+}$ , and  $Fe^{3+}$ . Additively colored crystals, which were in the  $F$  state, exhibited only  $Mn^{2+}$  and  $V^{2+}$  ESR signals. The 1500 °C heat treatment, performed prior to coloration, is known to convert  $Fe^{3+}$  into  $Fe^{2+}$ .<sup>12</sup> Iron was therefore thought to exist in the 2+ valence state, however,

its paramagnetic resonance spectrum consists of a very broad peak, 450 G wide, which is difficult to observe unless high concentrations are present. We were unable to directly observe this resonance.

After the crystals were photoconverted to the  $F^+$  state with ultraviolet light, iron was observed in the  $1^+$  valence state. A large  $F^+$  center resonance signal together with the  $Mn^{2+}$  and  $V^{2+}$  spectra were also observed. In order to detect the  $Fe^{1+}$  resonance, which consists of a single line occurring at  $g=4.15$ , measurements at temperatures of  $20^\circ K$  or lower were necessary due to the short spin relaxation time.<sup>13</sup> Using a heat treatment schedule similar to that used to obtain the states for the various curves in Fig. 1, both the  $F^+$  center and  $Fe^{1+}$  resonance signals were observed to decrease in essentially the same manner as the decrease of the  $500^\circ K$  thermoluminescence peak. After the crystals were heated above  $650^\circ K$ , no further luminescence was observed, and neither the  $F^+$  center nor  $Fe^{1+}$  ESR spectra could be detected, indi-

cating that the crystals had returned to their original  $F$  state. The crystals could be cycled between these states repeatedly. This fact was also observed in the previously reported optical absorption measurements.<sup>10</sup>

Owing to the correlation obtained between the ESR and thermoluminescence measurements, it is our conclusion that  $Fe^{2+}$  ions constitute the traps responsible for the  $500^\circ K$  glow peak. The conversion process



is driven to the right by light in the  $F$  band and to the left by the thermal release of electrons from the  $Fe^{1+}$  ions. A similar attempt to correlate changes in ESR signals with the glow curve peaks occurring below room temperature was unsuccessful. Except for a slight decrease in the  $F^+$  line, no change in the ESR spectrum was observed following heat treatments between  $77$  and  $298^\circ K$ .

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## Energy Bands in Boron Nitride and Graphite

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The tight-binding approximation has been applied for calculation of the band structure of planar hexagonal crystal layers of graphite and boron nitride. The theoretical width of the valence band of 15.9 eV in graphite and the distance between the centers of  $\pi$  and  $\sigma$  band of 5.3 eV as obtained in the present calculation are in good agreement with Chalkin's experimental work yielding 15 and 5 eV, respectively. For boron nitride, the width of the energy gap and the width of the valence band were calculated to be 4.9 and 6.8 eV, respectively.

### INTRODUCTION

Several authors<sup>1-5</sup> studied the electron structure of hexagonal boron nitride as early as 1950.

The studies are mainly made in comparison with graphite. According to these authors the width of the gap between the valence and conduction band in boron nitride is determined predominately by