

## Photoconductivity and luminescence of electron irradiated $\text{CaO}^{\dagger*}$

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We report an experimental investigation of the electronic structure of  $F$  and  $F^+$  centers in electron-irradiated  $\text{CaO}$  using the spectral response and temperature dependence of photoconductivity, with associated luminescence and fluorescence lifetime measurements made on the same samples. Photoconductivity and optical-absorption measurements were made over the spectral range from 2 eV (620 nm) to 4.5 eV (275 nm). Photoconductivity and fluorescence measurements were made over the temperature range from 65 to 350 K. The photoresponse of  $F^+$  centers increased sharply with increasing temperature between 210 and 300 K, where the zeroth moment,  $M_0$ , of the  $F^+$  luminescence was decreasing with increasing temperature. Below 200 K, photoconductivity from the  $F^+$  center was masked by photoconductivity from an unidentified impurity. The thermal activation energy for  $F^+$ -center photoconductivity was 0.24 eV. The photoresponse of  $F$  centers showed no significant temperature dependence between 65 and 300 K. The  $F$ -center photoresponse could be optically bleached at all temperatures between 77 and 300 K and, then, fully restored by  $\gamma$  irradiation at room temperature.

### I. INTRODUCTION

Oxygen-ion vacancies in alkaline-earth oxides have been found to trap either one or two electrons forming  $F^+$  and  $F$  centers, respectively.<sup>1</sup> Useful experimental techniques for studying the electronic structure of  $F$ -type centers in these materials include the spectral response and temperature dependence of photoconductivity and the temperature dependence of fluorescence. In general, thermal release of a free charge carrier from an excited  $F$ -type center competes directly with fluorescence decay.<sup>2</sup>

Recently it has been shown<sup>3,4</sup> that  $F^+$  centers in electron-irradiated  $\text{SrO}$  produce photoconductivity in a way reminiscent of  $F$  centers in alkali halides. In this paper we present the results of an experimental investigation of the electronic structure of both  $F$  and  $F^+$  centers in  $\text{CaO}$ .<sup>5</sup>  $\text{CaO}$  is the most convenient alkaline-earth oxide to use for this type of investigation because it can be obtained comparatively pure and because the  $F$  and  $F^+$  optical bands are well separated in energy.<sup>1</sup> Photoconductivity measurements on  $\text{MgO}$ ,<sup>6,7</sup> and  $\text{BaO}$ ,<sup>8</sup> containing  $F$ -type centers are more difficult to interpret because the  $F$  and  $F^+$  bands overlap in these materials. In  $\text{CaO}$ , the asymmetric  $F^+$  absorption band is located at 3.65 eV (340 nm) with a corresponding luminescence band centered at 3.35 eV (370 nm).<sup>9</sup> The  $F$  absorption band is located at 3.1 eV (400 nm) with luminescence bands at about 2.05 eV (605 nm).<sup>10,11</sup>

Detailed calculations of the electronic structure of the  $F$  center in alkaline-earth oxides have been presented recently,<sup>12</sup> including an account of lattice relaxation effects. These results can be compared

satisfactorily with the results presented here. No such detailed calculations for  $F^+$  centers are currently in the literature. We shall see below, however, that  $F^+$  centers in  $\text{CaO}$  appear to behave, so far as our experiments were concerned, similarly to  $F^+$  centers in  $\text{SrO}$  and  $F$  centers in alkali halides.

### II. EXPERIMENTAL DETAILS

Samples of  $\text{CaO}$  about  $10 \times 5 \times 2$  mm<sup>3</sup> in dimensions were cleaved from a boule (S/N 120-021172) which was supplied to us by Chen. The samples were irradiated at 77 or 195 K for several hours with 1.5-MeV electrons at an average current of about 5  $\mu\text{A}$ . The samples were warmed to room temperature for transfer to the photoconductivity cryostat. Before photoconductivity or optical measurements were made the samples were polished on a dry alumina impregnated lapping disk which gave the surfaces a good optical polish.

Photoconductivity measurements were performed in an apparatus which has been described in detail previously.<sup>13,4</sup> The samples were held between blocked plane parallel electrodes and were surrounded by dry helium exchange gas. Light from a xenon lamp was dispersed by a McPherson 218 monochromator and fell on the sample in the same direction as the applied electric field, which was typically about 500 V cm<sup>-1</sup>. The absolute value of the incident light intensity was measured to an accuracy of about 8%. Photocurrents, which were of the order of  $10^{-14}$  A, were detected with a Cary 401 vibrating reed electrometer used in the "rate of charge" mode.

For photoluminescence measurements, exciting

light from either a xenon or mercury lamp was dispersed by a Jarrell-Ash 82-410 monochromator. Emitted light was dispersed by a McPherson 218 monochromator and was detected with a thermoelectrically cooled RCA C31034 photomultiplier using conventional lock-in techniques and a PAR 128A lock-in amplifier. Fluorescence lifetime measurements were made with an optical arrangement similar to that used for the photoluminescence measurements. Pulses of exciting light with a halfwidth of about 25 nsec were produced by a Xenon Corp. air spark discharge lamp. The emitted fluorescence decay was photographed from the screen of a Tektronics 535A oscilloscope. Whenever necessary samples could be irradiated with  $\gamma$  rays from a  $^{60}\text{Co}$  source with a strength of about  $3 \times 10^4$  R/h.

### III. EXPERIMENTAL RESULTS

The main part of the experimental results concern the photoresponse of  $F$ -type centers in CaO. However, we have also investigated the temperature dependence of the luminescence intensity and the lifetime of the fluorescence from these centers as they relate to the photoconductivity. In Sec. III A the spectral dependence of the photoresponse is discussed and in Sec. III B the temperature dependence of the photoresponse and fluorescence are presented. Finally, in Sec. III C the effects of  $\gamma$  irradiation and optical bleaching of the samples are discussed.

#### A. Photoconductivity

So long as the mean range of the charge carriers is small compared to the thickness of the sample  $d$ , the photocurrent  $I$  excited in a sample located between plane parallel electrodes is given by the equation<sup>14</sup>

$$I = eN_0\eta(V/d)(\omega_0/d), \quad (1)$$

where  $e$  is the electronic charge,  $N_0$  is the number of photons incident on the sample per second,  $\eta$  is the free-electron yield per incident photon,  $V$  is the potential difference across the sample, and  $\omega_0$  is the mean range of the charge carriers in the direction of the applied electric field. Application of Eq. (1) requires that the photocurrent is proportional to both the applied electric field and the incident light intensity. The photoconductivity of  $F$  and  $F^+$  centers in CaO met these conditions within an experimental error of a few percent for the magnitude of light intensity and electric field used in our measurements. It is usual to collect the measurable quantities in Eq. (1) on one side of the equation to obtain a photoresponse  $\eta\omega_0$ , given by the equation

$$\eta\omega_0 = (I/N_0)(d^2/eV). \quad (2)$$

The photoresponse presented in this way is corrected for the incident light intensity and the parameter  $\eta$  contains the effects of the reflectivity  $R$  and the absorption constant  $\alpha$  of the sample. Specifically

$$\eta = \eta_T(1-R)(1-e^{-\alpha d}), \quad (3)$$

where  $\eta_T$  is the quantum efficiency for release of a free charge carrier per absorbed photon.

In Fig. 1, curve a, we show the photoresponse  $\eta\omega_0$  of an untreated sample of CaO at 77 K over the spectral range from 2.5 to 4.5 eV. It can be seen that the photoresponse was immeasurably small until the incident photon energy was at least 3.4 eV and that there was, then, a photoresponse band located near 3.8 eV. Subsequent  $\gamma$  irradiation of the sample at room temperature for several hours had little effect, except that the photoresponse below 3.0 eV was enhanced, although  $\gamma$  irradiation alone did not introduce any prominent photoresponse bands into the sample.

In Fig. 1, curves b and c, we show the photoresponse of a sample of CaO following irradiation at 77 K with 1.5-MeV electrons to a dose of approximately  $5 \times 10^{17}$  electrons  $\text{cm}^{-2}$ , and subsequent  $\gamma$  irradiation at room temperature for  $\sim 30$  min just prior to being mounted in the cryostat.

The effect of  $\gamma$  irradiation was to enhance the  $F$ -center photoresponse relative to the  $F^+$ -center

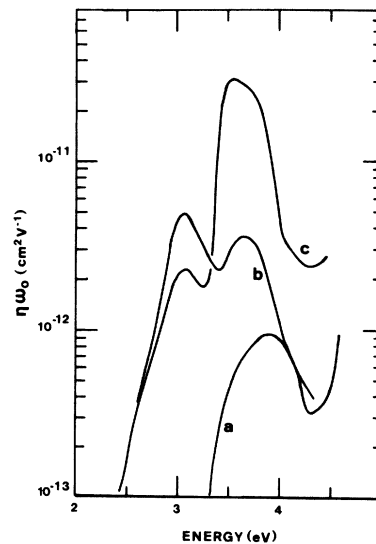


FIG. 1. Spectral dependence of the photoresponse  $\eta\omega_0$  for CaO. An untreated sample measured at 77 K, curve a; a sample which had been irradiated at 77 K with 1.5-MeV electrons to a dose of approximately  $5 \times 10^{17}$  electrons  $\text{cm}^{-2}$  and measured at 77 K, curve b; the same sample as curve b measured at 300 K, curve c.

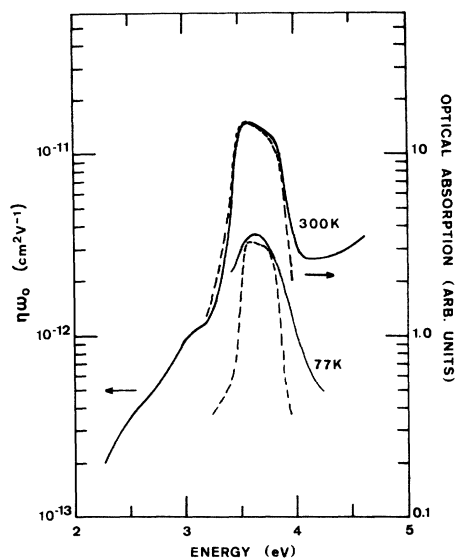


FIG. 2. Comparison of the spectral dependence of the photoresponse  $\eta\omega_0$  in electron-irradiated CaO, continuous curves, and the optical absorption of the  $F^+$  band in the same crystal, broken curves, at 77 and 300 K.

photoresponse as we discuss in detail in Sec. III C. Curves b and c show the photoresponse of the same sample measured at 77 and 300 K, respectively. The main features in the photoresponse were the nearly-temperature-independent band centered at 3.1 eV and the temperature-dependent band near 3.65 eV. Electron irradiation is known to introduce both  $F^+$  and  $F$  centers into CaO,<sup>15</sup> and by comparison of the spectral dependence of the photoresponse and optical absorption we shall show below that the photoresponse bands originate from  $F$  and  $F^+$  centers, respectively.

It can be seen in Fig. 1, curve c, that the photoresponse of an electron-irradiated sample was dominated at room temperature by the asymmetric band located near 3.65 eV. The continuous curve at the top of Fig. 2 shows the photoresponse at 300 K of an electron-irradiated sample in which the 3.1-eV band ( $F$  band) was further diminished by optical bleaching (see Sec. III C). The broken curve at the top of Fig. 2 shows the spectral dependence of the light absorbed in the same sample. The broken curve is, therefore, proportional to  $(1 - e^{-\alpha d})$  where  $\alpha$  is the absorption coefficient of the  $F^+$  band at 300 K. If we take it that the reflectivity of the sample and  $\eta_T$  remained constant over the  $F^+$  band, the close agreement between the two curves, which were normalized at 3.7 eV, shows that the photoconductivity at 300 K originated from  $F^+$  centers. However, the photoresponse of the sample and the spectral dependence of the absorption in the  $F^+$  band at 77 K are not similar, as can

be seen at the bottom of Fig. 2. Since there is no reason to suppose that the temperature dependence of  $\eta_T$  was a function of wavelength across the  $F^+$  band, we conclude that the photoconductivity of the sample at 77 K in the region of 3.7 eV originates mainly from an unidentified impurity.

Although the photoresponse band centered at 3.1 eV in Fig. 1, curve b, appears similar to the  $F$  band, it is partially masked by the presence of the 3.7-eV band and the background photoresponse. However, using the fact that the  $F$ -band photoresponse could be optically bleached at 77 K (see Sec. III C), we obtained the photoresponse of the  $F$  band over a comparatively wide spectral range. In Fig. 3, curve a, is shown the photoresponse at 77 K of a sample which had been irradiated to a dose of approximately  $3 \times 10^{17}$  electrons/cm<sup>2</sup>. Figure 3, curve b, shows the photoresponse of the same sample after being bleached for 2 h at 77 K with 3.1-eV light from a xenon lamp. As well as destroying the  $F$ -band photoresponse, bleaching also reduced the photoresponse generally between 2.5 and 4.5 eV. In order to obtain the  $F$ -band photoresponse, curves a and b were normalized at 4.5 eV and then subtracted to obtain the broken curve in Fig. 3. The broken curve, which repre-

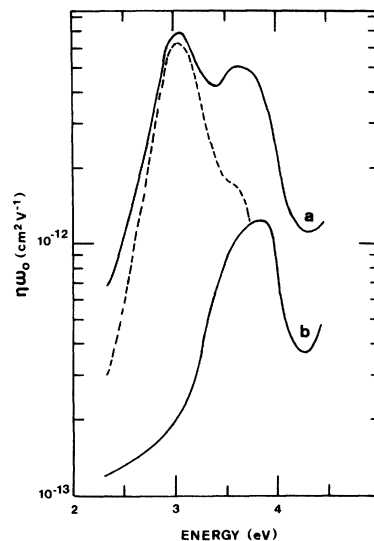


FIG. 3. Comparison of the spectral dependence of the photoresponse  $\eta\omega_0$  in electron-irradiated CaO before and after illumination in the  $F$  band. A sample which had been irradiated at 77 K with 1.5-MeV electrons to a dose of approximately  $3 \times 10^{17}$  electrons/cm<sup>2</sup>, curve a; the same sample as curve a after illumination for 2 h at 77 K with 400-nm light, curve b. Both sets of measurements were made at 77 K. To obtain the broken curve, which represents the spectral dependence of the  $F$ -band photoresponse, curves a and b were normalized at 4.5 eV and then curve b was subtracted from curve a.

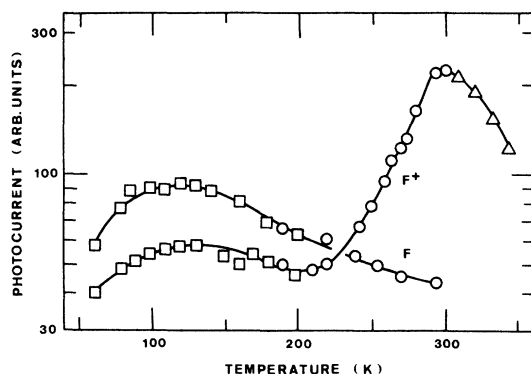


FIG. 4. Temperature dependence of the photocurrent produced by the  $F$  and  $F^+$  bands in CaO. The measurements were made with an incident photon energy of 3.1 and 3.65 eV, respectively. The various symbols indicate data collected in separate experiments.

sents the spectral dependence of the  $F$ -center photoresponse, has a peak at 3.1 eV and a half width of about 0.5 eV. This band was compared to and was found to be similar to the  $F$  band in additively colored CaO as reported by Modine.<sup>16</sup>

#### B. Temperature dependence of photoconductivity and fluorescence

It was seen in Fig. 1 that the  $F$ -band photoresponse was nearly independent of temperature between 77 and 300 K, whereas the  $F^+$ -band photoresponse increased significantly over the same temperature range. The detailed temperature dependence of the  $F$ - and  $F^+$ -band photoresponse between 65 and 350 K is shown in Fig. 4. The different symbols in Fig. 4 indicate measurements made during different experiments, which were made necessary in part by the sensitivity of the  $F$ -band photoresponse to bleaching. Between individual experiments the sample was  $\gamma$  irradiated at room temperature for  $\sim 30$  min in order to restore the  $F$ -band photoresponse as we discuss below in Sec. III C.

Below about 210 K, the photoresponse in the region of 3.7 eV originated mainly from an impurity band as we described in Sec. III A and it was only above 230 K that the  $F^+$  band was recognizable. The sharp increase in  $F^+$ -band photoresponse with increasing temperature beginning at 210 K is indicative of a thermally assisted ionization. The possibility that this increase was due to a thermally extended range of the charge carriers was ruled out because the photocurrent reached its maximum value within a fraction of a second (the response time of the detection system) and fell to zero equally fast upon removal of the incident light.<sup>2</sup> In addition, the increase in  $F^+$  photore-

sponse with increasing temperature was accompanied by a corresponding decrease in the fluorescence yield of the  $F^+$  emission, as can be seen in Fig. 5. In Fig. 5 we show the temperature dependence of the normalized zeroth moment  $M_0$  of the  $F^+$  emission measured on the same sample that was used for the photoresponse measurements, Fig. 4. For these measurements the luminescence was excited with the 3342-Å line from a mercury lamp. The  $F^+$  emission band is centered at 3.35 eV and  $M_0$ , which is proportional to the area under the emission curve, measures directly the number of centers involved in absorption and emission. In Fig. 5 it can be seen that  $M_0$  remained constant at temperatures between 77 and 120 K and then decreased continuously with increasing temperature up to 350 K, which was the maximum temperature obtained. When taken in conjunction with the photoresponse data, Fig. 4, we see that the decrease in  $M_0$  represented a decrease in the quantum efficiency for the  $F^+$  fluorescence. Notice that the increase in free-carrier yield from  $F^+$ -centers which should be apparent in Fig. 4 between 120 and 200 K was masked by the temperature-independent photoresponse from the 3.7-eV impurity band. The results presented in Fig. 5 are in substantial agreement with those of Evans *et al.*<sup>17</sup> which were obtained from neutron-irradiated CaO. These samples contained a preponderance of  $F^+$  centers. However, our results are somewhat dif-

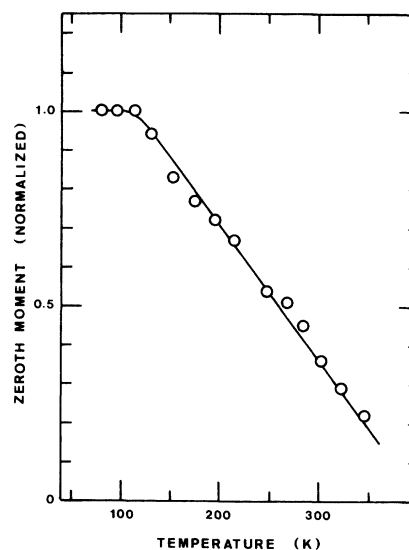


FIG. 5. Temperature dependence of the zeroth moment  $M_0$  of the  $F^+$  luminescence band in electron-irradiated CaO. The  $F^+$  luminescence band which was centered at 3.35 eV, was excited using the 3342-Å line from a mercury arc lamp. The measurements were made on the same sample used in obtaining Fig. 4.

ferent from those obtained by Henderson *et al.*<sup>9</sup> on heavily electron-irradiated CaO. Henderson *et al.* found an increase in  $M_0$  of about 20% between 100 and 230 K, followed at temperatures above 230 K by a decrease in  $M_0$  similar to that reported here. It is thought that the increase in  $M_0$  with increasing temperature occurred because of conversion of  $F$  centers to  $F^+$  centers by the exciting light.<sup>9,18</sup> A conversion of this kind has been observed by Kemp *et al.*<sup>19</sup> in additively colored CaO and by Chen *et al.*<sup>20</sup> in electron irradiated MgO. In our samples, however, the concentration of  $F$  centers was small (see Sec. III C below) and any  $F$  to  $F^+$  conversion which occurred would not significantly increase the concentration of  $F^+$  centers.

We also measured the temperature dependence of  $M_0$  for the  $F$ -band emission, which is located at 2.05 eV. These measurements which were made on additively colored samples supplied to us by Chen, were in close agreement with those obtained by Henderson *et al.*<sup>9</sup>  $M_0$  for the  $F$  emission decreased from 1.0 at 77 K to about 0.1 at 250 K. This decrease in  $M_0$  with increasing temperature was not matched by an increase in free-electron yield, Fig. 4.

The fluorescence lifetime of the  $F^+$  emission was measured on the same sample that was used for the photoresponse measurements, Fig. 4, and the luminescence results, Fig. 5. It was found that the fluorescence lifetime was at least as fast as the resolution of the apparatus, i.e., 30 nsec, over the whole temperature range from 77 to 300 K, in a region where we have seen the fluorescence yield was decreasing and the free-electron yield was increasing. A possible explanation of these results will be discussed in Sec. IV.

### C. Irradiation effects

We have described above how illumination into the  $F$  band tended to bleach the  $F$ -center photoresponse. The bleaching occurred with high efficiency at temperatures down to 77 K. It was also found that the spectral dependence of the photoresponse of a sample which had been electron irradiated several days before measurements were made, was similar to that of a bleached sample, which can be seen in Fig. 3, curve b. The  $F$ -band photoresponse could be restored by  $\gamma$  irradiating the sample at room temperature for ~30 min just before mounting it in the cryostat. The restoration of the  $F$ -center photoresponse by  $\gamma$  irradiation was quite dramatic. For example the photoresponse curve, Fig. 3, curve a, could be reproduced from the bleached or aged sample by  $\gamma$  irradiation for only a few minutes. Results similar to ours on aged samples were obtained by Roberts and Craw-

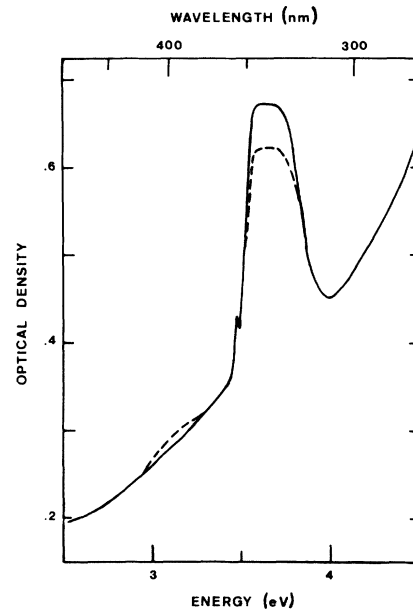


FIG. 6. Comparison of the intensity of the  $F^+$  band (3.65 eV) and the  $F$  band (3.1 eV) in CaO at 77 K before and after  $\gamma$  irradiation. The broken curve was measured before  $\gamma$  irradiation and the continuous curve was measured after  $\gamma$  irradiation at room temperature for 30 min. The sample which was 1.77 mm thick had previously been irradiated at 77 K with 1.5-MeV electrons to a dose of approximately  $5 \times 10^{17}$  electrons  $\text{cm}^{-2}$ .

ford<sup>7</sup> in electron irradiated MgO, in which  $\gamma$  irradiation was necessary prior to measurement in order to observe the  $F$ -center photoresponse.

In our samples, the increase in  $F$ -center photoresponse was not accompanied by an increase in  $F$ -center concentration, as measured by the optical absorption of the sample. In Fig. 6, the broken curve shows the optical absorption of a sample which had been electron irradiated and, then, stored several days at room temperature before measurement. It can be seen that the sample contained mostly  $F^+$  centers but that there is a small number of  $F$  centers also present. After the sample had been  $\gamma$  irradiated at room temperature for 30 min, the absorption spectrum shown as the continuous curve in Fig. 6 was measured. It can be seen that the  $F^+$  band was increased slightly by the irradiation while the  $F$  band was diminished. The effect of  $\gamma$  irradiation on our electron irradiated samples was, therefore, similar to the effect of ultraviolet light on the additively colored CaO samples used by Kemp *et al.*<sup>19</sup>

The increase in  $F$ -center photoresponse following  $\gamma$  irradiation of our samples was, therefore, not due to an increase in the number of centers, but due to an increase in the mean range  $\omega$  of the electrons released by the incident light. We es-

timate that the mean range was increased in this way by a factor of at least 30. The fact that the photoresponse in the spectral region of 3.7 eV was not increased by an equally large factor (see Fig. 3) may suggest that the charge carriers released at 3.7 eV are positive holes rather than electrons. A variation in the sign of the charge carriers released by incident light of different wavelengths has been observed previously in MgO, for example.<sup>6</sup>

The changes in photoresponse and optical absorption of our samples described above were only temporary. After several days the sample reverted to its equilibrium state. It is apparent that the trapping mechanisms operative in CaO samples containing  $F$ -type centers are quite complicated. However, one possible line of further investigation is the dependence of the photoresponse of  $F^+$  and  $F$  centers on the absolute and relative number of centers present.

The  $F^+$ -band photoresponse could not be optically bleached even at room temperature. It is already well known that the  $F^+$  absorption band cannot be bleached optically.<sup>1</sup> Figure 4 shows that at 77 K illumination of the  $F^+$  band does not produce free charge carriers so that no optical bleaching would be expected. Illumination at room temperature, which does produce free charge carriers, must produce a metastable state of the crystal which then returns to the initial state, i.e.,  $F^+$  centers, upon removal of the incident light. An alternative consideration is that the samples contain a significant concentration of oxygen vacancies, i.e.,  $F^{2+}$  centers. These would be expected to be strong electron traps and once having trapped an electron would become  $F^+$  centers.

#### IV. DISCUSSION

The electronic structure of the  $F$  center in CaO calculated by Wood and Wilson<sup>12</sup> is in substantial agreement with experimental results, including those reported here. The  $F$  band corresponds to an allowed transition from the  $^1A_{1g}$  ground state to the  $^1T_{1u}$  excited state. An electron in the  $^1T_{1u}$  state was calculated to be almost entirely outside the vacancy and when the center relaxed the  $^1T_{1u}$  state was within about 0.05 eV of the conduction band. Thermal ionization across such a small energy gap would be expected to occur below 65 K which explains why no significant temperature dependence in the  $F$ -band photoresponse is observed above 65 K and also why the  $F$  center could be optically bleached at 77 K. However, there is no simple explanation of the temperature dependence of the zeroth moment of the  $F$ -band emission in additively colored samples. It is worth reporting, however,

that the photoconductivity produced by illuminating additively colored samples containing a large number of  $F$  centers ( $\sim 10^{18}$  cm<sup>-3</sup>) had some unusual features. The photocurrent decreased as the illumination continued and, in addition, a transient dark current was produced which took several minutes to decay at 77 K. The fluorescence of these samples also contained a component with a lifetime of the order of minutes which appears related to the transient dark current described above. A similar transient dark current is produced by illumination of the  $F$  band in additively colored MgO.<sup>7</sup>

It has recently been shown<sup>4</sup> that the temperature dependence of the  $F^+$  band photoresponse in SrO could be analyzed quite well in terms of a two-level mode. In this model,<sup>2</sup> the free-carrier yield  $\eta_T$  is given by the equation

$$1/\eta_T - 1 = (\tau_0/\tau_R)e^{E_a/kT}, \quad (4)$$

where  $E_a$  is the activation energy for thermal ionization;  $\tau_R$  corresponds to a temperature-independent decay from an excited state;  $1/\tau_0$  is the preexponential frequency factor for thermal ionization;  $k$  is Boltzmann's constant; and  $T$  is the temperature. A similar analysis for the temperature dependence of the  $F^+$  band photoresponse in CaO is more difficult because the impurity photoresponse at 3.7 eV masks the  $F^+$ -band photoresponse below 210 K and, therefore, only a part of the free-carrier yield versus temperature curve could be obtained.

The experimental measurements of the photoresponse give us directly  $\eta\omega_0$ . In order to make use of Eq. (4) we assume that at 300 K an  $F^+$  center which had absorbed a photon was thermally ionized with unity probability, i.e., at this temperature  $\eta_T$  was equal to 1. In addition, we take it that the range  $\omega_0$  did not change over the temperature range from 230 to 280 K. This is not an unreasonable assumption over a small temperature range and has indeed been found to be the case in some alkali halides.<sup>21</sup> With these approximations we can use the data in Fig. 4 to obtain values for  $\eta_T$  as a function of temperature. The results are presented in Fig. 7, from which we obtain a value for  $E_a$  of 0.24 eV and a value for  $\tau_R/\tau_0$  of  $2 \times 10^4$ . Within the model our estimate of  $E_a$  is to an accuracy of about 20% and the estimate of  $\tau_R/\tau_0$  is within a factor of about 5. These results can be compared to values of  $E_a$  of 0.12 eV and  $\tau_R/\tau_0$  of  $5 \times 10^6$  for  $F^+$  centers in SrO.<sup>4</sup> If we take it that there is a trend in  $E_a$  for the alkaline-earth oxides, we would expect the  $F^+$  photoresponse in MgO to become observable only above room temperature and the  $F^+$  photoresponse in BaO to be observable at or below liquid-nitrogen temperature.

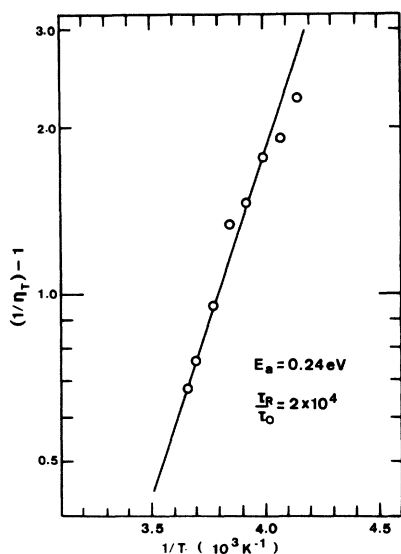


FIG. 7. Semilogarithmic plot of  $1/\eta_T - 1$  vs inverse temperature for  $F^+$ -center photoresponse in CaO. The data points were obtained from the experimental points shown in Fig. 4 as described in the text.

The fluorescence lifetime of an  $F$ -type center is expected to decrease with increasing temperature if the free-carrier yield is increasing. However, any change which occurred in the lifetime could not be detected by our apparatus because the radiative lifetime  $\tau_R$  was apparently shorter than 30 nsec. We notice that our estimate for  $\tau_R/\tau_0$  is not inconsistent with such a value of  $\tau_R$ . In the alkali halides,<sup>21</sup>  $\tau_0$  was found to be within an order of magnitude of  $10^{-12}$  sec. If  $\tau_0$  had a similar value in alkaline-earth oxides, and the results of Henderson *et al.*<sup>9</sup> suggest that this is probably the

case, our value of  $\tau_R/\tau_0$  would suggest a value for  $\tau_R$  of about 20 nsec.

Although photoconductivity from  $F$  centers in alkaline-earth oxides is generally expected in analogy to  $F$  centers in alkali halides, there is presently no satisfactory explanation of photoconductivity originating from  $F^+$  centers. One possible explanation<sup>22</sup> derives from a suggestion by Kemp and Neeley<sup>23</sup> that the  $A_{1g}$  ground state of the  $F^+$  center might be several eV below the top of the valence band of the host crystal. If this suggestion is correct, once the  $F^+$  center absorbed a photon it might, then, be energetically possible for an electron on one of the surrounding  $O^{2-}$  ions to jump into the vacancy. This process, which is a sort of charge transfer process, would leave a hole on the oxygen ion and if this hole were released, photoconductivity could occur. This explanation requires that the charge carriers be positive. From a somewhat involved experimental technique it appears, however, that the photocurrent excited by  $F^+$  centers in SrO is carried by electrons.<sup>3</sup> These experiments have not yet been performed on the  $F^+$  photoresponse in CaO. It is hoped that a definitive determination of the sign of the charge carriers excited from  $F^+$  centers in both SrO and CaO will be made in the near future.

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