PHYSICAL REVIEW B VOLUME 15, NUMBER 8 15 APRIL 1977

# Electron centers in single-crystal Al$_2$O$_3$[†]

K. H. Lee and J. H. Crawford, Jr.
*Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27514*

(Received 29 November 1976)

The two prominent absorption bands centered at 6.1 and 4.8 eV in neutron-bombarded Al$_2$O$_3$ single crystals have been investigated. Optical excitation into the 6.1 eV causes growth of bands at 5.4, 4.8, and 4.1 eV, whereas excitation into these latter bands causes growth of the 6.1-eV band. The oscillator strength of the 4.8-eV band was found to be in the range 0.5–1 as compared to a value nearly twice that for the 6.1-eV band. Excitation with 4.8-eV light produces an emission band at 3.75 eV and the yield and polarization of this emission as a function of the polarization of the exciting light was studied. This polarization behavior together with previous theoretical calculations is consistent with an assignment of the 4.8-eV band to the transition of the $F^+$ center. The oscillator strength ratio and the reciprocal relationship between the 4.8-eV band and the 6.1-eV band strongly indicate that the latter is associated with the $F$ center.

## I. INTRODUCTION

Recently,[1-5] much progress has been made in characterizing the defect structures in corundum ($\alpha$-Al$_2$O$_3$) crystals. As a result of investigations using electron spin resonance, optical absorption, and thermoluminescence, the identification of various hole centers is on firm footing. The $V^{2-}$ (an O$^-$ ion adjacent to an aluminum vacancy), the $V^-$ (two O$^-$ ions adjacent to an aluminum vacancy), and the $V_{\mathrm{OH}}^-$ (an O$^-$ ion adjacent to an aluminum vacancy which also has an OH$^-$ as a nearest neighbor) all absorb near 3.0 eV. The two-hole ($V^-$) centers anneal near 370 K, being transformed into $V^{2-}$ centers by the loss of a hole; the $V^{2-}$ centers thermally ionize at ~500 K and the $V_{\mathrm{OH}}^-$ at ~400 K. In contrast to these hole centers, the complementary electron trapping centers in $\gamma$-irradiated crystals are not so clearly identified. As in $\gamma$-irradiated MgO, there is no evidence of intrinsic electron centers such as $F^+$ (an oxygen-ion vacancy occupied by *one* electron) and $F$ (an oxygen-ion vacancy occupied by *two* electron) centers. Electron trapping apparently involves impurities such as Cr$^{3+}$,[3,4] although a careful ESR study reveals that Fe$^{3+}$ does not trap electrons in corundum crystals.[5]

Upon bombardment of Al$_2$O$_3$ crystals with particles (electrons,[6] neutrons,[7,8] energetic ions[9]) sufficiently energetic to displace lattice ions, several new absorption bands appear including a prominent band at 6.1 eV. Since similar treatment of MgO produces $F^+$, $F$, and $M$ centers, it might be expected that analogous simple defect centers are created in Al$_2$O$_3$. This paper reports our search for such centers. Fast neutron-irradiated corundum crystals have been studied by numerous investigators over that last two decades.[7-12] However, none of the ESR spectra and optical-absorption bands have yet been conclusively associated with the responsible defects. Recently, Turner and Crawford[12] have investigated the 6.1-eV absorption band through its relationship with $V_{\mathrm{OH}}^-$ center. They concluded that (i) the 6.1-eV band is due to an electron trapped at some defect produced by atomic-displacement processes, and (ii) the 6.1-eV band reflects the concentration of trapped holes rather than that of electron-trapping defects; i.e., the electron traps are more plentiful than stable hole traps. Another important, though less prominent, band in neutron-bombarded Al$_2$O$_3$ falls at 4.8 eV. On the basis of the Gibbs experimental studies,[13,14] Mitchell *et al.*[8] attribute this to either interstitial oxygen or the excitation of oxygen adjacent to aluminum vacancies. However, Tippins[15] has observed a Fe$^{3+}$ charge-transfer transition at 4.8 eV; thus Fe$^{3+}$ may very well explain the Gibbs results which are the main reason for Mitchell's assignment. In our paper, we will present evidence which indicates that the 4.8-eV band created by neutron irradiation is associated with the $F^+$ center and, because of its close and reciprocal relationship with the 4.8-eV band, that the 6.1-eV band may be associated with the $F$ center.

## II. EXPERIMENTAL

The uv grade Al$_2$O$_3$ crystals used in this study were purchased from the Linde Co. in the form of rods whose axes are perpendicular to the $C_3$ axis. Specimens were sliced from the rod perpendicular to the axis and the $C_2$ and $C_3$ axes were fixed by means of Laué x-ray scattering. Neutron irradiation was performed in the North Carolina State University Pulstar reactor which has a flux of $10^{13}$ reactor spectrum neutrons/cm$^2$ sec. Optical absorption was measured using a Cary $14R$ spectrophotometer. The emission detection system consisted of an RCA C 31034 photomultiplier tube mounted on a 0.5-m Jarrell-Ash monochromator with a dispersion of 16 Å/mm. A PAR model 113 amplifier and a PAR model 122 lock-in amplifier were used to control the gain of the signal. A reference signal for the lock-in amplifier was taken from a PAR model 125 A chopper. The polarized spectrum was obtained using a Polaroid HNP′D ultraviolet polarizing filter mounted upon a quartz window. Optical bleaching was accomplished with light from a 150-W xenon short-arc discharge lamp which was dispersed by a Bausch and Lomb high-intensity monochromator.

## III. RESULTS

After exposure to $5 \times 10^{16}$ neutrons/cm$^2$ the absorption spectrum has two prominent absorption bands centered at 6.1 and 4.8 eV and several weaker bands absorbing at 4.1, 3.5, and 2.7 eV all previously reported[7,8] to be produced by fast neutron bombardment. The 5.4-eV band was observed very clearly by using the difference curves between the $\vec{E} \parallel \vec{O}_3$ spectrum and the $\vec{E} \perp \vec{O}_3$ spectrum as reported by Mitchell *et al.*[8] Turner and Crawford[12] showed that $\gamma$ irradiation of neutron-irradiated $Al_2O_3$ increases the intensity of the 6.1-eV band which can then be reduced by subsequent 6.1-eV light bleaching. However, our study shows that even without $\gamma$ irradiation, the 6.1-eV band still can be bleached by 6.1-eV light. Figure 1(a) illustrates the effect of the 6.1-eV light bleaching for 2 min, as shown in the Fig. 1(a), while the 6.1-eV band decreases the 5.4- and 4.8-eV bands increase. The increase in the 5.4-eV band saturates after about 10 min of 6.1-eV light bleaching but the 4.8-eV band continues to grow and growth of a band at 4.1 eV is also observed. The 6.1-eV band can be restored while at the same time the 4.8-eV band can be bleached by irradiating with any of the following photon energies: 5.4, 4.8, and 4.1 eV. The effect of 4.8-eV light irradiation is shown in Fig. 1(b); the optical densities of the 5.4-, 4.8-, 4.1-, and 2.7- bands decrease and the 6.1- and 3.5-eV band increase. The 3.5-eV band does not behave consistently as the irradiation time increases and in some experiments it even showed a decrease. The optical densities of the bands can be recovered by uv irradiation which indicates the bleaching light changes the valence states of the defects produced by neutron irradiation rather than destroying the defects. In order to study the relationship of 6.1- and 4.8-eV bands through bleaching experiments, it is necessary to eliminate the contribution to the 4.8-eV region of the shoulder of the 5.4-eV band by bleaching the sample with 6.1-eV light for 10 h in order to build up the 4.8-eV band and eliminate the influence of the 5.4-eV band which saturates after a relatively short bleaching period. Figure 2 shows the optical densities of the 6.1- and the 4.8-eV band as a function of exposure time first to 4.8-eV light and then to 6.1-eV light. The intensity of 6.1-eV band increases with excitation into the 4.8-eV band and decreases with 6.1-eV light excitation, whereas the 4.8-eV band responds in the opposite manner, clearly suggesting an intimate and reciprocal relationship between them. The changes in the intensities of the 6.1- and the 4.8-eV bands after each irradiation were obtained using the initial intensities of these bands in Fig. 2 as the reference point. Plotted in Fig. 3 is the change of 6.1-eV band intensity as a function of the change in 4.8-eV band absorption; the curve shows that the 6.1- and the 4.8-eV bands bear a linear relation with each other. If we assume the change in

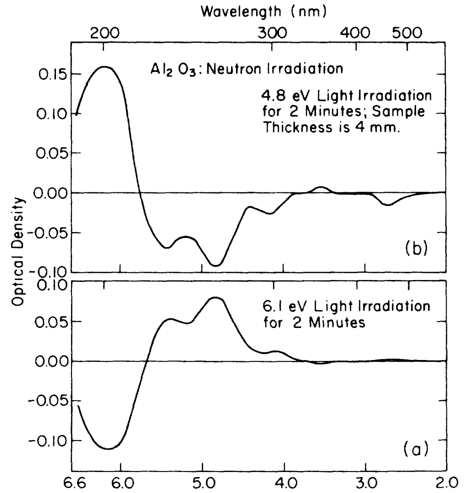

FIG. 1. (a) Effect of 6.1-eV light and (b) 4.8-eV light irradiation on the optical-absorption spectrum of a neutron-irradiated $Al_2O_3$ crystal ($5\times10^{16}$ neutrons/cm$^2$).

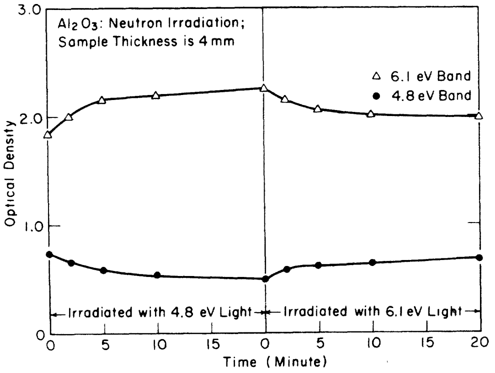

FIG. 2. Optical densities of the 6.1- and 4.8-eV band as a function of exposure time.

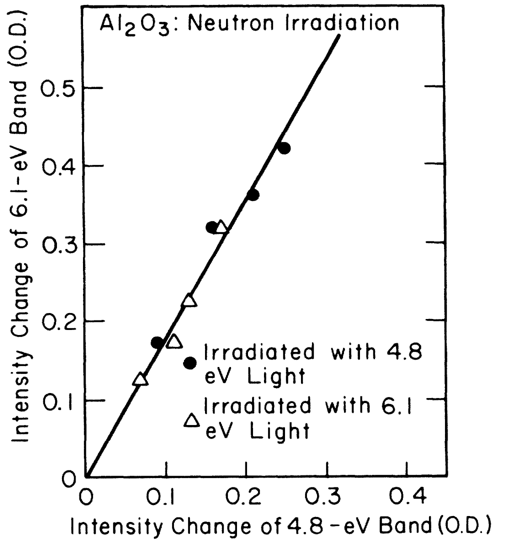

FIG. 3. Change of 6.1-eV band intensity as a function of change in 4.8-eV band absorption.

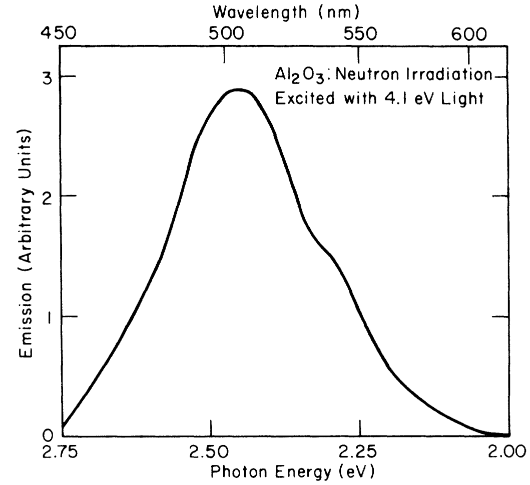

FIG. 5. 2.45- and 2.25-eV emission bands from a neutron-irradiated $Al_2O_3$ crystal.

the number of centers which are responsible for 6.1-eV band is the same as that for the 4.8-eV band, i.e., $\Delta N_{6.1} = \Delta N_{4.8}$, then from Smalkula's equation we get

$$(\Delta Nf)_{6.1}/(\Delta Nf)_{4.8} = (W_{1/2}\,\Delta\alpha)_{6.1}/(W_{1/2}\,\Delta\alpha)_{4.8} \ ,$$

where $f$ is the oscillator strength, $W_{1/2}$ is the half-width, and $\alpha$ is the absorption coefficient of the appropriate band. From Figs. 1 and 3, we find that $(W_{1/2})_{6.1} = 0.3$ eV, $(W_{1/2})_{4.8} = 0.27$ eV, and $\Delta\alpha_{6.1}/\Delta\alpha_{4.8} = 1.8$. Hence $f_{6.1} \cong 2 f_{4.8}$. If, as Turner and Crawford indicated,[12] the oscillator strength of the 6.1-eV band lies in the range 1 to 2, then that of the 4.8-eV band lies in the range of 0.5 to 1.

Figures 4–6 record the emission spectra of a Linde uv grade $Al_2O_3$ crystal which was given an exposure of $5 \times 10^{16}$ neutrons/cm$^2$. An emission band at 3.75 eV is observed upon exciting with 4.8-eV light, one at 2.45 eV is observed upon exciting with 4.1-eV light, and one at 2.25 eV is observed upon exciting with either 4.1- or 2.7-eV light. Prolonged excitation decreases the intensity of these emissions which indicates that the absorbing centers are being bleached by the excited light. The excitation spectrum for 2.25-eV emission band indicates that both the 4.1- and the 2.7-eV absorption bands are associated with the same defect complex. Excitation with 2.7-eV light does not affect the amplitude of this absorption band which

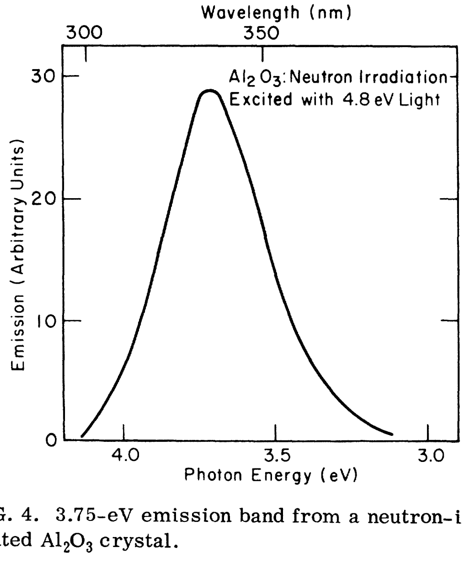

FIG. 4. 3.75-eV emission band from a neutron-irradiated $Al_2O_3$ crystal.

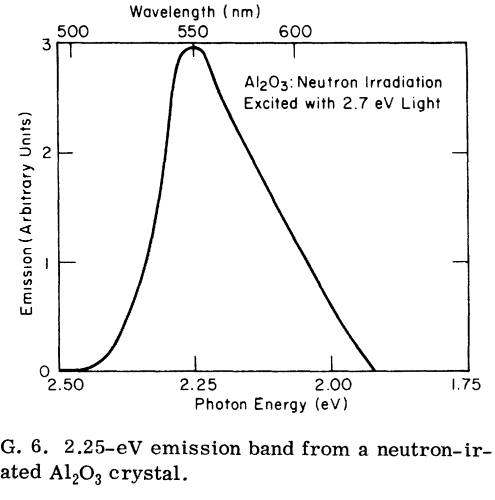

FIG. 6. 2.25-eV emission band from a neutron-irradiated $Al_2O_3$ crystal.

further suggests that the 2.7-eV band is due to a lower excited state which does not produce ionization. No luminescence resulting from excitation into the 6.1-eV band has yet been detected. An $S=\frac{1}{2}$, $g\simeq 2$ ESR signal which appears in the neutron irradiated sample has been investigated by exciting into various absorption bands. Upon exciting with either 4.8- or 5.4-eV light the intensity of this signal decreases and some of its intensity can be recovered upon irradiating into the 6.1-eV band. However, no linear relation of the $S=\frac{1}{2}$ signal with either the 5.4- or 4.8-eV band has been found. Nevertheless, this experiment definitely rules out the possibility that the $S=\frac{1}{2}$ signal is associated with 6.1-eV band, since enhancement of the 6.1-eV band is accompanied with a decrease of the $S=\frac{1}{2}$ signal. The 13-line ESR signal which was observed by La *et al.*[11] and attributed to the $F^+$ center is not observed in our samples indicating that if present it is below the level of detection.

## IV. DISCUSSION

Since irradiation into the 6.1-eV band results in bleaching, it is concluded that the parent electron center[12] is ionized by this particular optical transition. The symmetrical shape of the absorption band suggests that the electron is released by thermal ionization from a localized relaxed excited state near the conduction band rather than by direct ionization. This is a common behavior of the $F$ center in the alkaline-earth oxides and the alkali halides. The electron freed in the process can be captured at any one of a variety of traps as evidenced by the growth of bands at 5.4, 4.1, and 2.7 eV. The band at 4.8 eV also grows. However, there is evidence that its growth is not a result of electron capture: (i) $\gamma$ irradiation of a neutron irradiated crystal causes a relative decrease in absorption at this photon energy while the 6.1-eV band and other bands associated with electron and hole traps increase in intensity as can be seen in Fig. 1, Ref. 12; (ii) irradiating into the composite $V$ band at 3.0 eV produces an increase in absorption at 4.8 eV as the 6.1-eV band decreases as shown in Fig. 2, Ref. 11 (see also the dip at 4.8 eV in Fig. 4, Ref. 12); and (iii) $\gamma$ irradiation of a neutron bombarded ($5\times10^{16}$ neutrons/cm$^2$) crystal which had been heated above 600 K to ionize thermally $V_{\text{OH}}^-$, $V^-$, and $V^{2-}$ hole centers, causes a restoration of the trapped holes as well as an increase in the 6.1-eV band and a decrease of about one-half that amount in the 4.8-eV band.[16] These points of evidence together with the reciprocal relation between irradiation-induced changes in their intensities (Fig. 3) indicate that these two bands are associated with different charge states of the same defect and that the charge state producing the 4.8-eV absorption has one less electron than the state responsible for the 6.1-eV band which is also consistent with the behavior of the ESR mentioned above. Coupling this evidence with the ratio of oscillator strengths justifies the view that 6.1 eV is the transition energy of a two-electron center, and 4.8 eV is the transition energy of a one-electron center. In alkaline-earth oxides the well-known one-electron center,[17] the $F^+$, has an oscillator strength of 0.8 and the value for the $F$ center is nearly twice that. Therefore, it is tempting to conclude that these bands are transitions of the $F$ and the $F^+$ center. Although one might expect that the transition energy of the one electron center would be larger than that for the two-electron center, it is pointed out that the $F^+$ transition in MgO is 4.95 eV as compared to an $F$ transition of 5.05 eV.[18]

More-direct evidence for the nature of these centers can be obtained from the polarized excitation and emission spectra. These have been shown to be very powerful tools in the identification of anisotropic color centers.[19-21] The $F^+$ center in $\text{Al}_2\text{O}_3$ has $C_2$ symmetry, which causes the $2p$ states to split into $1B$, $2A$, and $2B$ states. La *et al.*[11] calculated the $F^+$ energy levels and found a transition ($1A\rightarrow 2B$) at 5.15 eV which is in reasonably good agreement with the observed value (4.8 eV). For the electric dipole transitions $1A\rightarrow 2B$ (absorption) and $2B\rightarrow 1A$ (emission), only $\pi$ transitions are allowed. The $F^+$ center in $\text{Al}_2\text{O}_3$ can occupy three equivalent sites and the $z$ axis ($C_2$ axis) of each site differs by 120° from the other. Figure 7 illustrates of the sample orientation with respect to both the incident light and the detection system; it also shows the orientation of the electric dipoles of the $F^+$ center. The intensity of the excitation and emission for various polarizations can be calculated from the following equation[19,20]:

$$I_{\mu\nu}=\rho\sum_i n_i\left|\hat{r}_i^{\beta_1}\cdot\hat{D}_\mu\right|^2\left|\hat{r}_i^{\beta_2}\cdot I_\nu\right|^2,$$

where $\rho$ is a constant, $n_i$ is the number of dipoles in the $\hat{r}_i$ orientation and $n_i$ is constant for the random distribution case, $\hat{D}_\mu$ and $\hat{I}_\nu$ are the polarized emission and excitation transition vectors, respectively, where $\mu,\nu=1$, 2, and 3 for the $\hat{x}$, $\hat{y}$, and $\hat{z}$ axes, respectively, and $\beta_1$ and $\beta_2$ can both refer to $\sigma,\pi_1,\pi_2$. For $\pi$ absorption and $\pi$ emission, the predicted intensities $\vec{C}_3\parallel\hat{x}$ and $\vec{C}_3\parallel\hat{y}$ are shown in Table I. The predicted and observed values for $\vec{C}_3\parallel\hat{x}$ and $\vec{C}_3\parallel\hat{y}$ of the polarized emission

$$I_{1u}/I_{2u}=(I_{11}+I_{13})/(I_{21}+I_{23}),$$

and polarized excitation

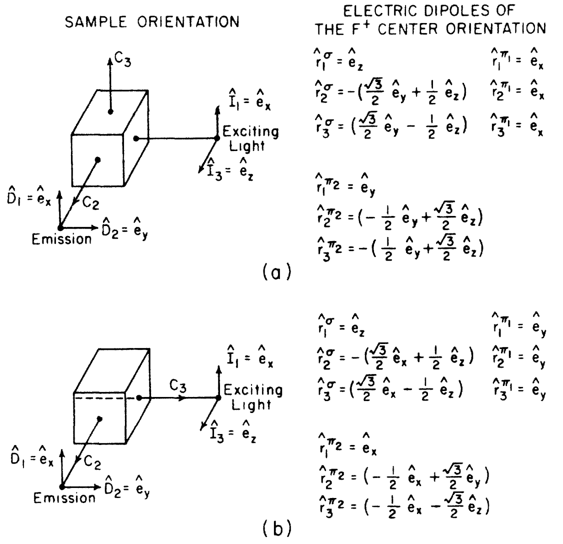

FIG. 7. Schematic illustration of the sample orientation with respect to both the incident light and the detection system and the orientation of the electric dipoles of the $F^+$ center of $Al_2O_3$ sample.

$$I_{u1}/I_{u3}=(I_{11}+I_{21})/(I_{13}+I_{23}),$$

are shown in Table II. Although the agreement is quite good for $\vec{C}_3\parallel\hat{y}$, the agreement for the $\vec{C}_3\parallel\hat{x}$ crystal orientation is not so convincing. The discrepancy for $\vec{C}_3\parallel\hat{x}$ may be due to the orientation variance between $\vec{C}_3$ axis of the crystal and $\hat{x}$ crystal and $\hat{x}$ axis of the center since the variance from $\vec{C}_3$ axis is more critical for $\vec{C}_3\parallel\hat{x}$ than for the $\vec{C}_3\parallel\hat{y}$ orientation. The orientation variance can not only be affected by errors in crystal alignment but also by distortion of the lattice by the center itself and it should be remembered that these defect centers are located in a region of relatively high lattice disorder, i.e., the displacement-cascade region engendered by a fast neutron collision. Therefore, the overall agreement between expectation and observation is considered reasonable.

As indicated above we have not yet found a luminescence associated with the 6.1-eV band upon excitation at room temperature although we did not look beyond 850 nm. In addition our polarizer cannot be used below 220 nm, and we are thus unable to look for optical anisotropy in this absorption band. Earlier studies by Mitchell *et al.*[8] suggest that this band is isotropic but the stacked plate polarizer which they used may not have had the necessary precision to rule out polarization completely. As in the case of the $F^+$ center some optical anisotropy might be expected depending upon the nature of the electronic states involved in the transition.

TABLE I. Intensity of polarized absorption and emission.

| | $I_{11}$ | $I_{13}$ | $I_{21}$ | $I_{23}$ |
|---|---|---|---|---|
| $\vec{C}_3\parallel\hat{x}$ [Fig. 7(a)] | $3\rho n$ | $1.5\rho n$ | $1.5\rho n$ | $0.375\rho n$ |
| $\vec{C}_3\parallel\hat{y}$ [Fig. 7(b)] | $1.125\rho n$ | $0.375\rho n$ | $1.5\rho n$ | $1.5\rho n$ |

The question remains as to why irradiating into the 4.8-eV band enhances the 6.1-eV band. If the former is the $F^+$ band, electron release is not expected.[17] However, the 5.4- and 4.1-eV bands associated with trapped electrons extend under the 4.8-eV band and excitation at this energy would release electrons from the traps which are known to be optically bleachable. Hence the apparent bleaching of the 4.8-eV band could result from the capture of optically released electrons by the $F^+$ center to form $F$ centers. Alternatively, it is possible that, instead of corresponding to the $F^+$ band, 4.8 eV is the energy of a charge transfer transition in which an electron is transferred from a near-neighbor $O^{2-}$ onto the $F^+$ center. Thermal dissociation of this bound exciton to release the hole could result in the creating of an $F$ center and a hole trapped elsewhere. If this explanation is correct, the analysis of polarized absorption and emission spectra given above would no longer be relevant even though the charge transfer transition may also produce polarized absorption and emission. Typically, however, the oscillator strength of charge-transfer transitions is ~0.1,[22] and the width of a charge transfer band is nearly independent of temperature whereas the 4.8-eV band is narrower at low temperature.[8] Therefore, this alternative explanation is much less preferable to the first one which identifies the 4.8-eV band with the $F^+$ band and explains its bleaching by the capture of electrons released from traps by $F^+$ band light.

A band at 5.4 eV is also observed in $\gamma$-irradiated $Al_2O_3$.[7] Turner and Crawford[12] have attributed this

TABLE II. Intensity ratio of polarized excitation or polarized emission.

| | $\vec{C}_3\parallel\hat{x}$ [Fig. 7(a)] | | $\vec{C}_3\parallel\hat{y}$ [Fig. 7(b)] | |
|---|---|---|---|---|
| | predicted | observed | predicted | observed |
| $\frac{I_{1u}}{I_{2u}}$ | 2.4 | 1.5 | 0.5 | 0.5 |
| $\frac{I_{u1}}{I_{u3}}$ | 2.4 | 1.3 | 1.4 | 1.6 |

band to a transition of $Cr^{2+}$. A band near this position is also reported in $\gamma$-irradiated ruby.[23, 24] Although release of holes from $V_{OH}^-$ centers results in the annihilation of this band with the emission of $Cr^{3+}$ $R$-line luminescence, there is some difficulty with this assignment since no appreciable increase in the concentration of $Cr^{3+}$ during the annealing of $V_{OH}^-$ has been detected by ESR measurements.[5] It seems likely that the 5.4-eV band observed in neutron irradiated crystals has the same origin as in $\gamma$-irradiated crystals. From their behavior the 4.1- and 2.7-eV bands appear to be associated with a trapped electron. The amplitude of these bands grow relative to other bands with increasing neutron integrated flux suggesting that the center responsible is an aggregate-type center. Further work is necessary to decide the identity of the defects responsible for both the 5.4- and 4.1-eV bands.

## V. SUMMARY

The oscillator strength, theoretical calculations, and polarized excitation, and emission data are consistent with the assignment of the 4.8-eV band to $F^+$ centers created by neutron bombardment. Interconversion of the 6.1- and 4.8-eV bands can be accomplished by irradiating into the respective band. The oscillator-strength ratio and the reciprocal relation between the 4.8- and 6.1-eV bands are strong indications that they are associated with the same defect in different charge states. If the assignment of the 4.8-eV band to the $F^+$ center is correct, the 6.1-eV band must be the $F$ band.

## ACKNOWLEDGMENT

The authors are grateful to Dr. F. J. Steinkruger for irradiating the crystals in the North Carolina State University Pulstar reactor.

---

†Supported by the Materials Research Center, University of North Carolina under Grant No. DMR 72-03024 from NSF.

[1] F. T. Gamble, R. H. Bartram, C. G. Young, O. R. Gilliam, and P. W. Levy, Phys. Rev. **134**, A589 (1964).

[2] R. T. Cox, Solid State Commun. **9**, 1989 (1971).

[3] T. J. Turner and J. H. Crawford, Solid State Commun. **17**, 107 (1975).

[4] K. H. Lee, G. E. Holmberg, and J. H. Crawford, Solid State Commun. **20**, 183 (1976).

[5] K. H. Lee, G. E. Holmberg, and J. H. Crawford (unpublished).

[6] G. W. Arnold and W. D. Compton, Phys. Rev. Lett. **4**, 66 (1960).

[7] P. W. Levy, Phys. Rev. **123**, 1226 (1961).

[8] E. W. J. Mitchell, J. D. Rigden, and P. W. Townsend, Philos. Mag. **5**, 1013 (1960).

[9] G. W. Arnold, G. B. Krefft, and C. B. Norris, Appl. Phys. Lett. **25**, 540 (1974).

[10] F. T. Gamble, R. H. Bartram, C. G. Young, O. R. Gilliam, and P. W. Levy, Phys. Rev. **138**, A577 (1965).

[11] S. Y. La, R. H. Bartram, and R. T. Cox, J. Phys. Chem. Solids **34**, 1070 (1973).

[12] T. J. Turner and J. H. Crawford, Phys. Rev. B **13**, 1735 (1976).

[13] P. Gibbs, I. B. Cutler, and J. L. Bates, Bull. Am. Phys. Soc. **2**, 300 (1957).

[14] P. Gibbs, *Conference on the Kinetics on High-Temperature Processes*, edited by W. D. Kingery (Wiley, New York, 1959), p. 21.

[15] H. H. Tippins, Phys. Rev. B **1**, 126 (1970).

[16] F. J. James and J. H. Crawford (unpublished).

[17] A. E. Hughes and B. Henderson, in *Point Defects in Solids*, Vol. I, edited by J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York–London, 1972), p. 381.

[18] Y. Chen, J. L. Kolopus, and W. A. Sibley, Phys. Rev. **186**, 865 (1969).

[19] P. P. Feofilov, *The Physical Basis of Polarized Emission* (Consultants Bureau, New York, 1961).

[20] C. R. Riley, S. I. Yun, and W. A. Sibley, Phys. Rev. B **5**, 3285 (1972).

[21] K. H. Lee and W. A. Sibley, Phys. B **12**, 3392 (1975).

[22] B. DiBartolo, *Optical Interactions in Solids* (Wiley, New York, 1968), p. 416.

[23] T. Maruyama and Y. Matsuda, J. Phys. Soc. Jpn. **19**, 1096 (1964).

[24] G. E. Arkhangelshii, Z. L. Morganshtern, and V. B. Neustruev, Phys. Status Solidi **22**, 280 (1967).