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Low-temperature fluorescence in sapphire

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The polarized fluorescence band at 3.0 eV which can be produced by photoexcitation of the 6.1-eV F band in high-purity α-Al_2O_3 has been studied over the temperature range 4.4–300 K. The centroid and zeroth moment of the band remain relatively constant with increasing temperature, but the half-width follows a hyperbolic cotangent relation with an effective frequency of 345 cm^{-1}. A Huang-Rhys factor of 14.7 is estimated for the band. After pulse excitation at 4.4 K the fluorescence decays following a curve which can be analyzed as the sum of two exponentials with lifetimes of 24 and 160 ms, respectively. Both the lifetime and the intensity of each component are temperature dependent between 15 and 40 K. Above 50 K the intensity decays following a single exponential with a lifetime of 34 ms. A schematic electronic structure is suggested for the F center, which is consistent with the experimental results and the expected nature of the center.

I. INTRODUCTION

Single-crystal samples of sapphire are readily available of sufficient purity that they show almost no optical absorption (absorption coefficient, $\alpha < 2$ cm^{-1}) over the spectral range from 2 to 6.5 eV. Since many $3d$ ions have strong charge-transfer transitions in the region of 6 eV,[1] these can only be present at concentrations of a few parts per million at most, which is confirmed by more detailed analysis. In many instances, however, similar samples grown under reducing conditions exhibit a pronounced optical-absorption band with a peak near 6.1 eV and a full width at half maximum intensity (FWHM) of 0.68 eV.[2] This band, or its low-energy tail, has been observed in "as-received" samples for many years.[3,4] The same band can be produced by deliberate additive coloration[5] and also by particle bombardment.[6,7] The evidence is now strong that the 6.1-eV band is mainly due to F centers, that is, to oxygen ion vacancies, each of which has trapped two electrons.

The identification of anion vacancy centers in sapphire has been made difficult by the absence of any confirmed electron-spin-resonance signals, although a 13-line spectrum has been reported in heavily neutron-irradiated samples.[8] In addition to the evidence from thermochemical coloration, the strongest evidence for the identification of the 6.1-eV band comes from its relation to the absorptions of the F^+ center (an anion vacancy which has trapped only one electron). Optical excitation of the 6.1-eV band produces a large photoconductivity,[2] and results in the appearance of two other bands at 4.8 and 5.4 eV, respectively,[2,7] which are thought to be due to the F^+ center. Because of the low site symmetry of an oxygen vacancy (C_2), the excited p-like states of the F^+ center are expected to be split into three components by the local crystal field. The ordering of these components and hence the ordering of the polarized optical-absorption bands resulting from electron transitions from the ground state have been predicted on the basis of a point-ion model calculation by La *et al.*[8] The correct ordering and polarization properties are found for the 4.8 and 5.4-eV F^+ bands, which have, therefore, been assigned to the $1A \rightarrow 1B$ and $1A \rightarrow 2A$ transitions, respectively.[9] The $1A \rightarrow 2B$ transition near 6.0 eV is thought to be obscured by the 6.1-eV absorption, which is always present. It appears, then, that bleaching the 6.1-eV band produces F^+ centers by the trapping of one of the F-center electrons elsewhere in the lattice. Not all F centers can be bleached at one time, however, even at 4 K, possibly because of insufficient numbers of electron traps, or because a dynamic equilibrium is established due to partial overlap of the F band and the band associated with the electron trap.[2]

Optical excitation of the 6.1-eV band produces a luminescence band with a peak at 3.0 eV and a FWHM of 0.36 eV.[10,2,11] This photoluminescence band is seen in all samples exhibiting the 6.1-eV absorption band, although it is relatively weak in neutron-irradiated samples.[12] It has been shown that the excitation spectrum of the emission follows closely the spectral dependence of the 6.1-eV absorption band.[2] Measurements at temperatures between 77 and 300 K have shown that after pulsed excitation the 3.0-eV emission intensity decays exponentially with a lifetime of 34 ms,[10,11] which is independent of temperature over the range investigated. It has recently been shown that the fluorescence decay is more complicated below 77 K.[13] In some samples much longer-lived phosphorescence is also observed near room temperature,[10,14] which is associated with a thermoluminescence peak at 270 K.[15]

The new results presented in this paper include details of the temperature dependence of the fluorescence lifetime and intensity of the 3.0-eV emission below 77 K, an analysis of the band-shape moments of the 3.0-eV band at low temperature, and the temperature dependence of the width of the 3.0-eV band between 4 and 300 K. In the Discussion section a comparison is made between the *F*-band emission in sapphire and other oxides and a model is suggested to explain the new features observed in the fluorescence measurements.

II. EXPERIMENTAL

The results presented here were obtained from ultraviolet-grade single-crystal samples of α-Al_2O_3 which were obtained from Crystal Systems, Inc. (CS), Adolf Meller, Inc. (AM), Insaco, Inc. (IN), and Linde. The CS samples were grown in the Schmidt-Viechnichi technique, the AM and IN samples were grown in adaptations of a Bridgman furnace, and the Linde samples were grown by the Czochralski technique. All the samples except the Linde samples showed the 6.1-eV absorption band when received, Fig. 1. The Linde samples were subsequently irradiated near room temperature with approximately 5×10^{17} fast neutrons, which introduced the 6.1-eV band, as well as the F^+ bands at 4.8 and 5.4 eV, Fig. 1. Usually the crystal boules are grown in a vacuum or in an argon atmosphere and the defects are, therefore, introduced thermochemically during growth. In order to remove the 6.1-eV band, the samples must be heated in an oxidizing atmosphere to over 1350 °C.[2,7] Although no comprehensive analyses were performed on the samples, analyses did show that V, Mn, Cr, and Fe ions were present at levels of a few parts per million.

The samples were approximately $15\times10\times1$ mm^3 in dimensions and were oriented so that the crystallographic *c* axis lay approximately parallel to the major dimension. Prior to each set of measurements the samples were heated to 500 °C in order to reestablish equilibrium[15] and then quenched to room temperature. The samples were attached to a holder which was surrounded by helium exchange gas and which could be cooled to 4 K in an Oxford Instruments continuous-flow helium cryostat.

In all measurements the 3.0-eV emission was excited using light from a 60-W deuterium lamp, which was focused on the sample through an interference filter with a peak transmission at 200 nm and with a bandpass of 17 nm. In steady-state measurements, the emitted light was dispersed by a McPherson 218 0.3-m grating monochromator and detected with an RCA C-31034 photomultiplier tube cooled to −20 °C. The output of the photomultiplier was measured using an electrometer, and the data corrected for the spectral dependence of the detection system. For fluorescence-lifetime measurements the exciting light was mechanically chopped to produce pulses a few ms wide and separated by about 80 ms. The rise and fall time of the pulses was less than 1 ms. The emitted fluorescence was passed through a Corning CS-0-52 cutoff filter and detected with an EMI 9813 B photo multiplier tube whose output was displayed on the screen of a Tektronics 7603 oscilloscope. Measurements were made from photographs of the oscilloscope screen.

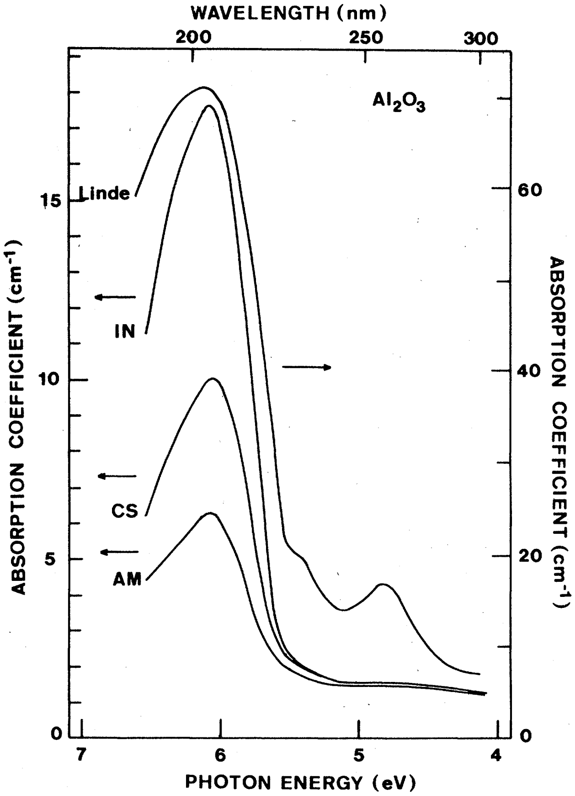

FIG. 1. Optical-absorption spectra of high-purity, single-crystal sapphire at 297 K. The IN (Insaco, Inc.), CS (Crystal Systems, Inc.). and AM (Adolf Meller, Inc.) samples were thermochemically colored during growth. The Linde sample had been irradiated near room temperature with approximately 5×10^{17} fast neutrons. Note that the right-hand scale refers to the Linde sample. The bands at 4.8 and 5.4 eV are due to F^+ centers and the large band at 6.1 eV is mainly due to *F* centers.

III. EXPERIMENTAL RESULTS

A. 3.0-eV luminescence

The emission spectra excited in a CS sample by unpolarized 6.1-eV light at 20 K are shown in Fig. 2. It has been shown previously that the excitation spectrum of this emission follows closely the spec-

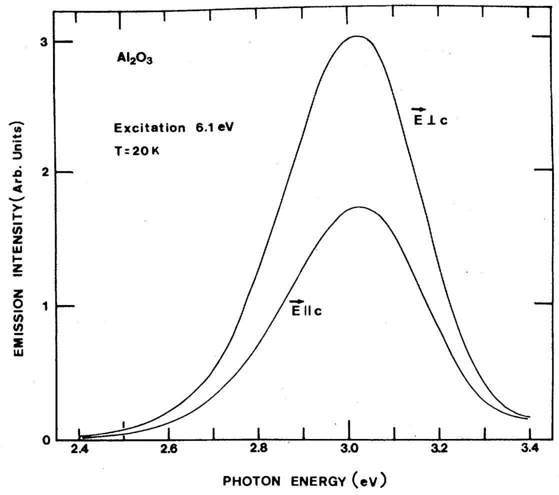

FIG. 2. Polarized emission spectra from a CS sample at 20 K. The excitation was centered at 200 nm with a bandwidth of 17 nm.

tral dependence of the F band.[2] The emitted light is plane polarized with the maximum intensity occurring when the electric vector is perpendicular to the c axis of the crystal ($E\perp c$) and the minimum occurring when the electric vector is parallel to the c axis ($E \parallel c$) as shown. Since the symmetry axis of the F center is in a plane perpendicular to the c axis of the lattice, it can be seen that the emission is preferentially polarized with the electric vector along the axis of the center. The degree of polarization for the direction of emission shown $\langle 1\bar{1}02\rangle$ is $E\perp c/E\parallel c \sim 1.7$, and was found to be independent of temperature between 4 and 55 K.

The emission band is slightly skewed towards the low-energy side, so that although the maximum emission at 20 K occurs at 3.00 eV, the band centroid is at 2.97 eV, and is the same for both polarization directions. The band centroid was found to be almost independent of temperature between 4 and 300 K. The zeroth moment of the band, which is proportional to the relative quantum efficiency of the emission, was found to be fairly constant for the 4–120 K range, but decreased by about 20% in the 120–300 K region. The decrease was consistent with a nonradiative process with an activation energy of about 0.06 eV.

B. Temperature dependence of bandwidth

The 3.0-eV luminescence band has a FWHM of 0.36 eV at low temperatures. This relatively large width, which is common in F-type centers, is due to the strong interaction between the F-center electron and the spectrum of normal modes of vibration of the surrounding ions. As the temperature increases, the width $W(T)$ is observed to increase due to this interaction as can be seen in Fig. 3. The same temperature dependence was observed for both polarization directions, and could be described by

$$W^2(T) = W^2(0)\coth(\hbar\bar{\omega}/2kT)\,, \tag{1}$$

where $W(0)$ is the FWHM at low temperature and $\bar{\omega}$ represents an average over the frequencies of the normal vibrational modes coupled to the emitting electronic state. The solid line in Fig. 3 is a computer fit of Eq. (1) to the data points with $W(0) = 0.361\,(2)$ eV and $\hbar\bar{\omega} = 345 \pm 20\ \text{cm}^{-1}$. This value for $\hbar\bar{\omega}$ is close to the value found in a similar way for the F^+ center in α-Al_2O_3 (340 cm^{-1}) as might be expected.[2]

C. Huang-Rhys factor

The shape of a broad emission band such as that observed here is due to the nature and strength of the electron-lattice interaction. If linear coupling is assumed, a convenient dimensionless measure of its strength is the Huang-Rhys factor, S, which is related to the second moment of the band $\langle E^2\rangle$ by $S = \langle E^2\rangle/(\hbar\bar{\omega})^2$, where $\langle E^2\rangle$ is defined as in Table I. Using the experimental value of $\langle E^2\rangle$ and the value of $\hbar\bar{\omega}$ from above, a value for S of 14.7 is obtained. It is worth noting that if the bandshape were Gaussian, $\langle E^2\rangle = W^2(0)/8\ln 2$, from which a value of S of 12.8 would be obtained. The fact that this value is within 15% of the experimental value is an indication of how close the 3.0-eV band shape is to Gaussian.

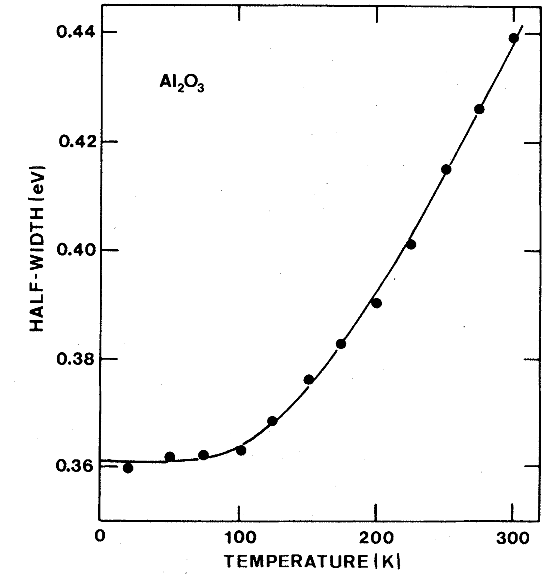

FIG. 3. Temperature dependence of the full width at half maximum intensity of the 3.0-eV emission band. The solid line is a fit of Eq. (1) to the experimental data points, with $\hbar\omega = 345\ \text{cm}^{-1}$ and $W(O) = 0.361$ eV.

TABLE I. Moments of the band-shape function[a] $f(E)$ for the 3.0-eV emission at 20 K.

	Moment	Value
Zeroth	$\sum_i f(E_i)\Delta E$	1[b]
First[c]	$\bar{E}=\sum_i E_i f(E_i)\Delta E$	2.97 eV
First about $\bar{E}$	$\langle E\rangle=\sum_i (E_i-\bar{E})f(E_i)\Delta E$	4.32×10^{-6} eV
Second about $\bar{E}$	$\langle E^2\rangle=\sum_i (E_i-\bar{E})^2 f(E_i)\Delta E$	0.0269 (eV)[d]

[a] Determined from the measured intensity $I(E_i)$ using $f(E_i)\propto I(E_i)/E_i^4$.

[b] Normalized.

[c] Band centroid.

[d] Reference 2.

The size of the Huang-Rhys factor gives an indication of the possibility of observing a zero-phonon line in the emission since the ratio of the total intensity in the zero-phonon line to the total intensity in the phonon-assisted portion of the band is proportional to $\exp(-S)$. It is generally recognized that if S exceeds about 6, the zero-phonon line will not be observable even at the lowest temperatures, and since in our case $S\sim15$, no zero-phonon line is expected, and none has so far been detected.

If it is assumed that the same effective vibronic frequencies occur in the emitting and ground states, a semiclassical configuration coordinate diagram can be constructed from which the difference between the absorption and emission energies, ΔE, can be found from $\Delta E=\hbar\bar{\omega}(2S-1)$. ΔE is usually called the Stokes shift. Using our experimental values of S and $\hbar\bar{\omega}$, a value for ΔE of 1.23 eV is obtained which is much less than the observed value of 3.1 eV. This result suggests that emission occurs from an excited state closer to the ground state than the level into which the electron was excited during absorption at 6.1 eV. A similar conclusion can be drawn on the basis of the relatively long lifetime of the emission, which we discuss in more detail below.

D. Lifetime measurements

In Fig. 4 we show a semilogarithmic plot of the total intensity in the 3.0-eV emission as a function of time, following pulse excitation with 6.1-eV light at temperatures of 4.4, 30.5, and 75 K, respectively. Figure 4 shows data obtained from an IN sample but similar data were obtained from the CS, AM, and neutron-irradiated samples. It can be seen that at 75 K the emission intensity decays following closely a single exponential with a lifetime of 34 ms, which is in agreement with previous measurements.[10,11] Below 50 K the decay curve, $I(t,T)$, is more complicated, but can be closely fitted by the sum of two decaying exponentials with temperature-dependent lifetimes and preexponential factors, i.e.,

$$I(t,T)=A(T)\exp[-t/t_1(T)]+B(T)\exp[-t/t_2(T)]\,. \quad (2)$$

Other possible time dependences were considered, such as might be expected for a second-order process, for example, but none of these possibilities fit the experimental data as closely as Eq. (2). The continuous lines in Fig. 4 are computer fits of Eq. (2) to the data points, from which the

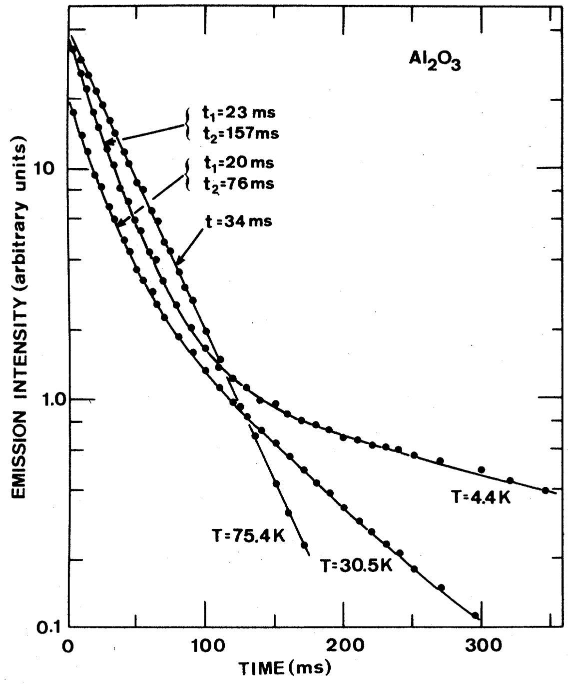

FIG. 4. Temperature dependence of the decay of the 3.0-eV fluorescence in an IN sample following pulse excitation with 6.1-eV light. The solid lines are computer fits of Eq. (2) to the data points. The curve for $T=30.5$ K has been shifted down to avoid overlap. It should coincide with the $T=4.4$ K curve at $t=0$.

lifetimes shown in Figs. 4 and 5 were found. The error bars in Fig. 5 were determined from the computer fits and the estimated experimental error in determining the emission intensity, which increases as the intensity decreases, i.e., for long t, where t_2 is mainly determined. The fraction of the total intensity contained in the two lifetime components can be estimated from the product of the factors A or B and the corresponding lifetimes, and is shown in Fig. 6. In summary the following conclusions can be drawn from the data shown in Figs. 5 and 6. At helium temperature the decay of the 3.0-eV emission intensity contains two exponentially decreasing components, with lifetimes of 160 and 24 ms, respectively. About 75% of the total intensity is contained in the shorter-lived component and 25% in the longer-lived component. Between 15 and 40 K the magnitude of the longer lifetime decreases to 34 ms at the higher temperature, while the total intensity in this component increases to 100%. The magnitude of the shorter lifetime also decreases over the same temperature range, and the intensity in this component falls to zero.

Measurements were made to determine whether the lifetime and intensity data depended on the polarization of the emission. Within the bounds of the errors shown in Figs. 5 and 6, neither the lifetimes nor the relative values of A and B depended on the polarization. Measurements were also made to determine whether different lifetime components were contained in different spectral regions of the 3.0-eV band. Again no measurable effect could be detected.

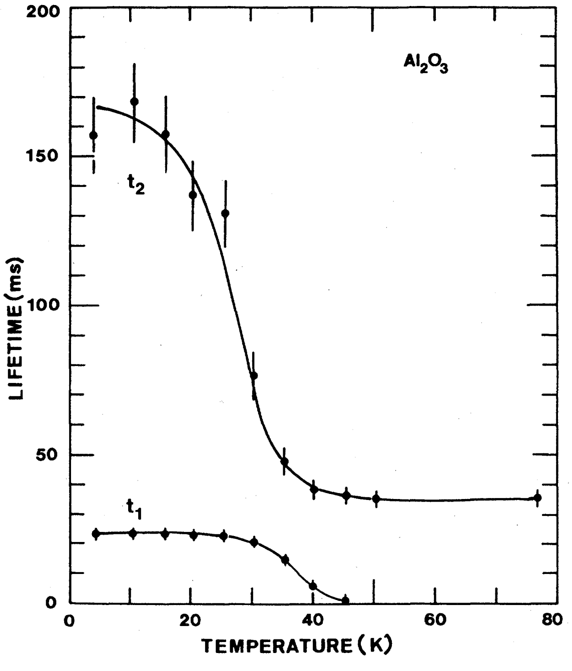

FIG. 5. Temperature dependence of the two lifetime components of the 3.0-eV fluorescence in an IN sample. The data were obtained from computer fits of Eq. (2) to experimental measurements such as those shown in Fig. 4. The errors are mainly due to uncertainties in the intensity measurements.

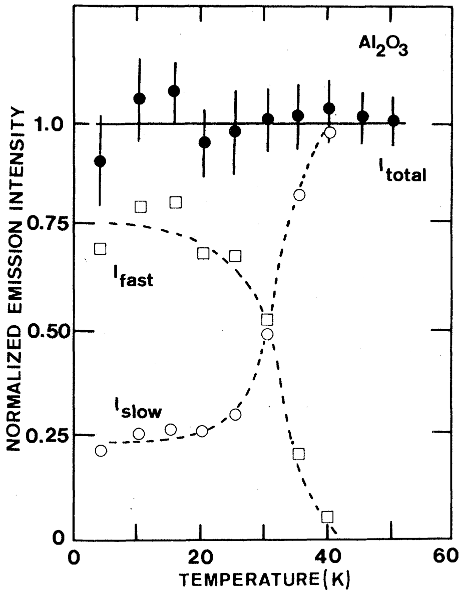

FIG. 6. Temperature dependence of the total intensity in the 3.0-eV fluorescence following pulse excitation, compared with the intensity in each of the two lifetime components. I_{fast} and I_{slow} refer to the components with $t_1 = 24$ ms and $t_2 = 160$ ms at 4.4 K, respectively. (See Fig. 4.)

IV. DISCUSSION

As we discussed in the Introduction the evidence is now very strong that the 6.1-eV absorption and the 3.0-eV emission are due to the F center. The positions of the first nearest-neighbor Al^{3+} ions surrounding the F center in α-Al_2O_3 are shown in Fig. 7, where the C_2 local symmetry of the center is clearly apparent. The ground state of the center is expected, therefore, to be ^1A and the main absorption occurs when an electronic transition occurs to a ^1p-like excited state. Although the C_2 symmetry of the crystal field would be expected to split a ^1p-like state into three components of $1A$, $1B$, and $2B$ character, only one F band is observed, in contrast to the three F^+ bands which are seen.[9] Although the reason for this difference is not definitely known, a possible explanation is suggested by the fact that photoconductivity is observed from the F band even at low temperatures (~10 K). Thus, the excited ^1p-like state involved in the absorption must be close to or even in the conduction band and we can conjecture that the corre-

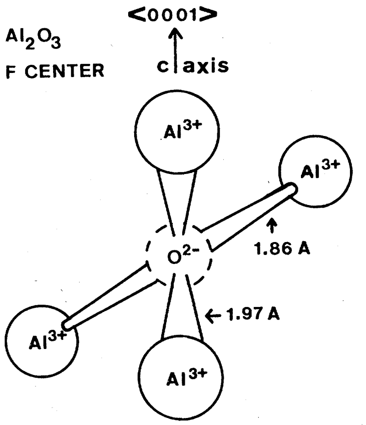

FIG. 7. Positions of the four nearest-neighbor Al^{3+} ions surrounding an oxygen vacancy in the corundum lattice.

sponding wave function is so extended that even in the unrelaxed configuration of the center the local symmetry is not important in determining its properties. Supporting evidence for this conclusion is that the emission from F centers in neutron-irradiated sapphire, in which the defects are formed in cascades, is concentration quenched, whereas the emission from F^+ centers in the same samples is not affected.[12]

As we have seen above, at the lowest temperatures two lifetime components are observed in the emission, both of which are much longer-lived than is expected for an allowed electric dipole transition (~10^{-8} s). The transition is, therefore, largely forbidden and the most obvious reason is that the emitting state is a spin triplet. This is known to be the case for the F luminescence in other oxides such as CaO, for example.[16] On the basis of the experimental value of the Huang-Rhys factor, the Stokes shift is expected to be about 1.23 eV, whereas a value of 3.1 eV is found. We suggest, then, that the emitting state is ^3p-like and is located about 1.6 eV below the ^1p-like state in the relaxed configuration of the F center, and that electrons fall into this state as a result of nonradiative decay. The measured lifetime is probably due to admixture of the singlet state into the lower-placed triplet state. It would be very useful if information about this emitting state could be obtained from excited-state ESR measurements.

The C_2 crystal field might be expected to split a relatively compact ^3p-like state into three components of ^31A, ^31B, and ^32B character, and we suggest that the observed two lifetime components are a result of this splitting. The character of the lowest-lying emitting state cannot be uniquely determined from our polarization measurements, but we can be certain that this state does not have uniquely $1A$ character, since in this case no intensity would be observed with $E \parallel c$, whereas, in fact, substantial emission is observed, Fig. 2. We conclude, then, that the emitting states have mainly B character. On the basis of these considerations an energy level diagram for the F center is proposed as shown in Fig. 8. As far as we can tell there is no radiative decay from the ^1p-like state to the ground state, which might be expected to occur at about 4.25 eV (290 nm). The splitting between the two lowest-lying triplet components determines the temperature-dependent properties of the fluorescence between 4 and 55 K. We assume that the uppermost component with mainly $1A$ character is not involved in the emission because of the polarization measurements and because no observable change in fluorescence properties is observed between 55 and 300 K. It appears, then, that this uppermost level is a considerable fraction of an eV above the lower-lying components, and we have, therefore, suggested in Fig. 8 that it lies more than 0.2 eV higher. Also, since the total fluorescence intensity does not change between 4 and 55 K there must be no nonradiative transitions to the ground state, which are accessible for these temperatures. The measurements are to be explained, therefore, in terms of a three-level model, the properties of which have been investigated in considerable detail previously.[17,18] One conclusion from these studies is that if the populations of the two emitting levels are in thermal equilibrium, only one lifetime component is observed in the fluorescence. We must assume, then, that at the lowest temperatures the transition rates between the two components due to phonon interactions are so slow that the levels are essentially independent. As the temperature increases above 15 K the populations in the two levels become gradually thermalized and a single lifetime of 34 ms is finally observed. From the temperature dependences of the lifetimes, Fig. 4, we can estimate that the two levels are separated by about 0.03 eV. At the low-

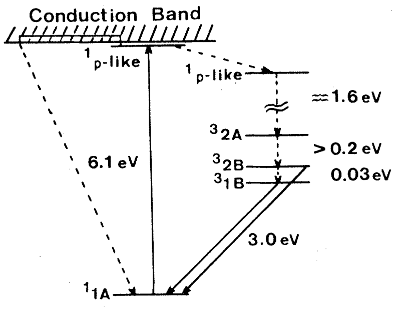

FIG. 8. Schematic representation of the energy levels of the F center in sapphire.

est temperatures the measurements indicate that about 75% of the emission occurs from the lower component and 25% from the upper, which is a measure of the nonradiative coupling to the ^1p-like state.

It is worth noting that the experimental data can be explained using an alternative model involving the action of a metastable electron trap. This model has been discussed in some detail elsewhere.[14] This possibility is worth considering because of the low-temperature photoconductivity which is observed. The long-lived component in the luminescence decay could, therefore, be due to the slow release of electrons into the conduction band from these traps. To distinguish between the two possibilities the low-temperature lifetime of the photoconductivity needs to be measured. This is not an easy measurement because of the relatively small photocurrent, but measurements are underway to determine it.

Finally, we note that the behavior of the fluorescence observed here has been seen in other systems such as interstitial hydrogen atoms in KCl and RbCl doped with I^- ions.[19] The red emission from these systems contains two lifetime components, one of the order of 10^{-6} s and the other about 10^{-8} s. The accepted interpretation for this system is similar to that described above. The longer-lived component which is dominant at low temperatures is thought to be due to a transition from an excited quartet state to the doublet ground state, and the change in the relative intensities of the two components as the temperature increases is suggested to occur when thermal excitation to a slightly higher doublet state takes place.

We should like to emphasize that it would be very useful if excited state ESR could be performed on the α-Al_2O_3 system. Apart from giving information about the metastable excited states, it would also give vital information about the structure of the defect itself.

ACKNOWLEDGMENT

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