

Temperature dependence of fluorescence yield and lifetime of F^+ centers in SrO

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The excited states of the F^+ center in neutron- or proton-irradiated SrO have been studied by measuring the temperature dependence of the yield and lifetime of the F^+ fluorescence over the temperature range from 5 to 140 K. Both the fluorescence yield and lifetime decrease in two stages; one over the temperature range from 5 to 60 K, and the other over the range 60 to 140 K. The results are interpreted in terms of a three-level model of the F^+ center which is suggested by recent theoretical work. The lowest radiative level, which has a lifetime of 0.42 μsec , is found to be 0.05 eV below the conduction band. Another level is found only 0.005 eV above this radiative level. In order to account for the results, nonradiative decay to the ground state appears to occur from this second level.

I. INTRODUCTION

The F^+ center in SrO consists of an oxygen-ion vacancy which has trapped a single electron.¹ Production of F^+ centers by incident neutrons or protons² is comparatively efficient, whereas production by high-energy electrons is inefficient even at low temperatures.³ The reason for this inefficiency seems to be related to the instability of isolated interstitial oxygen ions in SrO. It has so far not been possible to produce the two-electron center, the F center, by particle irradiation of SrO and it is necessary to resort to additive coloration at high temperature in an atmosphere of strontium vapor.⁴ The fact that the F center is not formed, however, makes it possible to study F^+ centers in proton- and neutron-irradiated SrO without the complicating presence of F centers.

The asymmetric and slightly flat-topped F^+ absorption band which occurs near 3.1 eV is due to a ${}^2A_{1g} \rightarrow {}^2T_{1u}$ transition of the F^+ center.⁵ A recent calculation using a model which includes the effects of the electronic structure on ions neighboring the defect, the electronic and ionic polarization of the lattice, and lattice distortion, indicates strong coupling of the F^+ -center electron to A_{1g} and T_{2g} vibrational modes, with considerably weaker coupling to E_g modes.⁶

Excitation into the F^+ band produces a blue-green luminescence centered at 2.5 eV,^{5,7} with a full width at half maximum intensity of 0.34 eV at 5 K.⁸ This emission is seen in both proton- and neutron-irradiated material. The radiative lifetime of the F^+ luminescence is 0.42 μsec ,⁸ which is considerably longer than might be expected for an allowed transition from a $2p$ -like excited state to a $1s$ -like ground state, and which is reminiscent of the relatively long lifetime of the F center in alkali halides.⁹ The model calculation referred to earlier

suggests that the reason for the long lifetime is that although excitation places the F^+ electron into a ${}^2T_{1u}$ level, subsequent relaxation of the center lowers a ${}^2A_{1g}^*$ level below the T_{1u} level. Low-temperature radiative decay to the ground state becomes, therefore, parity forbidden. The forbidden nature of the transition could be partially lifted, however, by mixing of the ${}^2T_{1u}$ and ${}^2A_{1g}^*$ states by odd-parity phonons, which is a mechanism originally suggested for the F center in alkali halides by Swank and Brown.⁹ Unlike the case of the F center in KCl, however, it will be shown below that the fluorescence from F^+ centers in SrO decreases in two stages as the temperature increases from 4 to 140 K. A corresponding decrease is also observed in the lifetime of the F^+ emission over the same temperature range.

Photoconductivity measurements have shown that there is a relaxed excited state of the F^+ center about a tenth of an electron volt below the bottom of the conduction band.³ This figure was deduced assuming that the mobility of the charge carriers was independent of temperature over the range 55 to 120 K. This experimental value is in fairly good agreement with the calculated value of about 0.2 eV.⁵

Useful information about the nature of the electronic structure of the F^+ center in SrO is obtained from the temperature dependence of the fluorescence intensity and lifetime, which is the subject of this paper. It will be shown that the experimental results can be satisfactorily explained in a manner which is generally consistent with current models of the electronic structure of the F^+ center.

II. EXPERIMENTAL CONSIDERATIONS

The fluorescence measurements described here were made on proton- or neutron-irradiated single

crystal samples of SrO. One sample was cleaved from a boule obtained from W. and C. Spicer, Ltd., and was irradiated at 77 K to a dose of about 1.5×10^{17} protons/cm². The other sample was grown at Oak Ridge National Laboratory and was neutron-irradiated at room temperature.

A 150-watt xenon lamp was used to excite the F^+ luminescence. The energy of the incident photons was selected using a suitable interference filter plus a wide band Corning filter to reduce the stray light. The emitted luminescence was dispersed by a McPherson 218 0.3-m monochromator with a grating blazed at 300 nm and detected by an RCA C-31034 photomultiplier tube cooled to -30°C . The incident light was chopped using a mechanical chopper and the signal was synchronously detected using a PAR 128A lock-in detector. For excitation measurements the incident light was dispersed by a Jarrell-Ash 0.25-meter grating monochromator.

The F^+ fluorescence was excited by a pulse of light with a width at half maximum intensity of about 25 nsec, which was obtained from an air spark discharge lamp manufactured by Xenon Corporation. The emitted fluorescence was detected by a photomultiplier and photographed from the screen of a wide-band oscilloscope, either a Tektronics 535A or 7603. The fluorescence data was analyzed and replotted on semilogarithmic paper. The lifetimes were obtained from the slope of these plots.

III. EXPERIMENTAL RESULTS

A. Photoluminescence

The photoluminescence spectrum excited by 3.1 eV light in proton-irradiated SrO is shown in Fig. 1. No other emission was detected over the wavelength range from 450 to 900 nm. At 12 K the F^+ emission band is almost symmetrical, although there is a slight asymmetry due to a low-energy tail. The peak of the emission occurs at 2.50 eV and at 12 K the full width at half maximum intensity is 0.34 eV. An identical band is observed in neutron-irradiated material. The excitation spectrum of the 2.5 eV band is shown as the lower curve in Fig. 2. The curve is plotted on semi-logarithmic paper for ease of comparison with the light absorbed into the F^+ band in the same sample, which is shown as the upper curve in Fig. 2. The optical density at the peak of the F^+ absorption band in this sample was 0.18. The similarity between the two curves in Fig. 2 strongly suggests that the 2.5 eV band is due to a transition of the F^+ center.

As the temperature of the sample was raised above 12 K the total intensity of the F^+ luminescence decreased as can also be seen in Fig. 1.

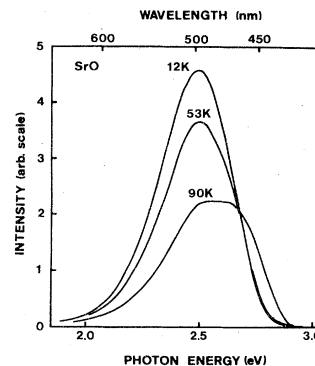


FIG. 1. Photoluminescence spectrum emitted by F^+ centers in SrO. The sample had been irradiated at 77 K to a dose of approximately 5×10^{17} protons/cm².

This decrease is significant even over the temperature range from 12 to 50 K. For temperatures above 80 K, a shoulder at 2.7 eV becomes apparent on the 2.5 eV band, Fig. 1. A similar temperature dependence was observed in the emission from the neutron-irradiated sample, although at any temperature the relative size of the 2.5 and 2.7 eV bands was different in this sample. In addition the 2.7 eV band can be observed in some unirradiated samples, in which the 2.5 eV band is not observed. For these reasons it appears that the 2.7 eV band is not directly associated with the F^+ center. The presence of the 2.7 eV band, however, complicates the analysis of the F^+ luminescence intensity. In spite of this, it can be seen in Fig. 1 that as the temperature increased, the F^+ emission decreased, and that it was substantially quenched by the time the temperature reached 90 K. In order to obtain detailed information about the temperature dependence of the F^+

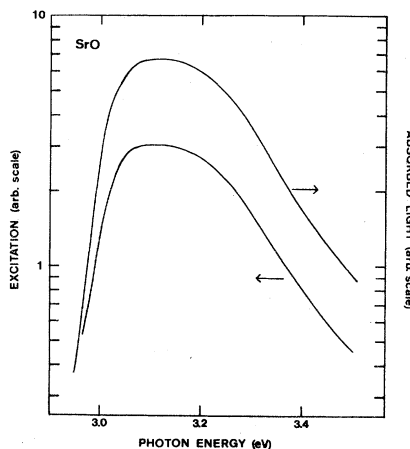


FIG. 2. Comparison of the excitation spectrum of the F^+ center luminescence with the light absorbed in the F^+ absorption band in the proton-irradiated sample at 77 K.

emission it is necessary to subtract the 2.7 eV band, which can be done using an analysis described below. It will be recalled that the photoconductivity due to F^+ centers was observed to grow rapidly as the temperature increased above 60 K.³ This behavior is consistent with a model in which the excited F^+ electron either can be thermally excited into the conduction band or can return to the ground state of the center by radiative decay. A model which accounts for the experimental observations in detail is described below in Sec. IV.

B. Temperature dependence of F^+ center fluorescence

In order to obtain detailed information about the temperature dependence of the 2.5-eV F^+ center fluorescence the contribution of the 2.7 eV band must be subtracted from the total fluorescence. This subtraction was performed by computer. Inspection of the 12 K curve of Fig. 1, and measurements made on the neutron-irradiated sample indicated that the F^+ emission could be reasonably well represented by a Gaussian function, as can be seen in Fig. 3. This fitting procedure slightly overestimates the high-energy part of the curve, and underestimates the low-energy tail, but gives the area under the curve to within a few percent. The low-energy tail is present to some extent even when the F^+ band is quenched, so it is not clear whether it is entirely due to F^+ centers in any case. Since we are concerned here with the area under the emission spectrum, which is proportional to the quantum efficiency of the F^+ fluorescence, and not with details of the band shape, and since the Gaussian gives a good approximation to this area, it was decided to fit the curves to two Gaussians: one centered near 2.5 eV and the other centered near 2.7 eV to take into account the im-

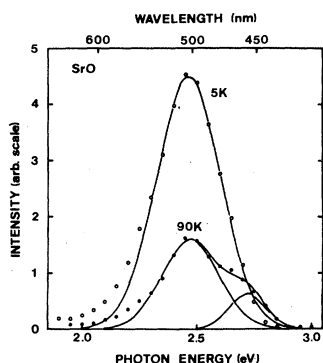


FIG. 3. A fit of two Gaussian curves to the F^+ center luminescence band in neutron-irradiated SrO. The circles and dots are the experimental points and the solid lines are the fitted curves. The two components which make up the curve for $T=90$ K are also shown.

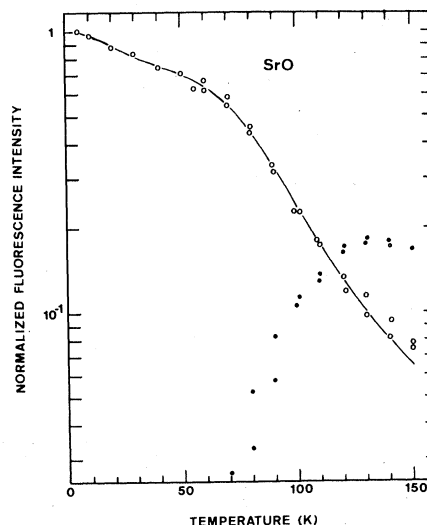


FIG. 4. Temperature dependence of the zeroth moment of the F^+ center luminescence in neutron-irradiated SrO (circles). The solid line is a fit of Eqs. (3) and (5) to the data points with $E_1=0.044$ eV and $E_2=0.004$ eV. The dots show the data for the 2.7 eV impurity band.

purity emission. The result of the fit to a typical curve (90 K) is also shown in Fig. 3, along with the resulting decomposition into two bands.

In Fig. 4 we show the temperature dependence of the F^+ fluorescence as determined from the experimental data using the fitting procedure described above. The circles give the data points and the continuous line is a fit of these data to a model which is described in Sec. IV. The measurements made on the proton-irradiated sample gave similar results. The most important result of the analysis is that it shows that the F^+ fluorescence is thermally quenched in two stages, one over the temperature range from 4 to 60 K and the other from 60 to 140 K. The temperature dependence of the 2.7 eV band is also shown in Fig. 4 for comparison. It can be seen that although this band generally grows as the 2.5 eV band decays, there is no significant growth until the temperature is above 60 K. It will be recalled that it is above this temperature that the photoconductivity grows rapidly too.

C. Fluorescence lifetime

The lifetime of the F^+ fluorescence was measured over the temperature range from 10 to 120 K. Typical results which were replotted from the photographs are shown in Fig. 5. At the lowest temperature the fluorescence decays exponentially with a lifetime of $0.42 \mu\text{sec}$. A small fluorescence intensity which decays more rapidly is also apparent. As the temperature of the sample in-

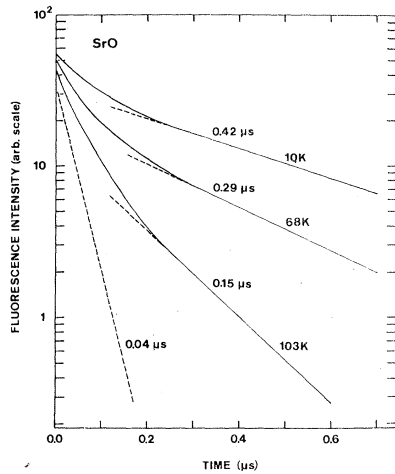


FIG. 5. Replotted F^+ center fluorescence lifetime data. The curve for $T=103$ K is also shown decomposed into two components, one with $\tau=0.04$ μs and the other with $\tau=0.15$ μsec . The resolution of the apparatus was approximately 0.04 μsec .

creased above 10 K, the fluorescence curves began to appear more complicated than a single first-order process, as can be seen in Fig. 5. However, these curves can be accurately decomposed into two first-order processes with different lifetimes. Other possibilities were tried, such as a single second-order process, for example, in which case $1/(\text{intensity})^{1/2}$ would be proportional to t , but none of these fit the data as closely as the sum of two decreasing exponentials. One of these components, which contains nearly all the intensity at low temperatures, is assigned to the F^+ fluorescence, and has a lifetime which decreases from 0.42 μsec at 10 K to 0.15 μsec at 103 K. This fluorescence is also assigned to the F^+ center on the basis of its temperature dependence, which is similar to the temperature dependence of the 2.5-eV F^+ band, Fig. 4, measured in the steady-state experiments. The details of the F^+ fluorescence lifetime are shown in Fig. 6. The other component in the fluorescence has a lifetime of approximately 0.04 μsec , which is close to the response time of the apparatus. Both the lifetime and the intensity of this component are approximately independent of temperature. The origin of this fluorescence is not clear, but it is probably due to an impurity fluorescence in the same spectral region as the F^+ band. At 10 K the intensity in this impurity fluorescence is less than 0.1 of the intensity in the F^+ center emission.

IV. DISCUSSION

It is clear from the temperature dependence of the F^+ center fluorescence, Fig. 3, that a two level

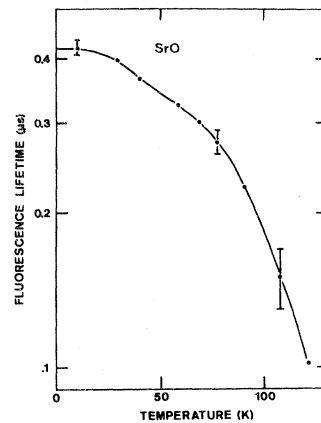


FIG. 6. Temperature dependence of the F^+ center fluorescence lifetime in proton-irradiated SrO. The solid line is a fit of Eqs. (3) and (5) to the experimental results with $E_1=0.057$ eV and $E_2=0.007$ eV.

model similar to that used for the F center in alkali halides⁹ will not be suitable here. The major new feature observed for the F^+ center in SrO is the two stage thermal quenching of the fluorescence, which suggests that a three level model should be considered. Such a model is also indicated by theoretical calculations which put the lowest ${}^2A_{1g}^*$ level close in energy to the lowest ${}^2T_{1u}$ level, with both a fraction of an electron volt below the conduction band of the host lattice. We, therefore, consider the energy-level diagram and the rate processes shown in Fig. 7, where levels 1 and 2 represent the levels of mainly ${}^2T_{1u}$ and ${}^2A_{1g}^*$ character, respectively. As has been suggested previously, levels 1 and 2 are actually expected to be combinations of ${}^2T_{1u}$ and ${}^2A_{1g}^*$ levels which could be suitably mixed by odd-parity phonons.

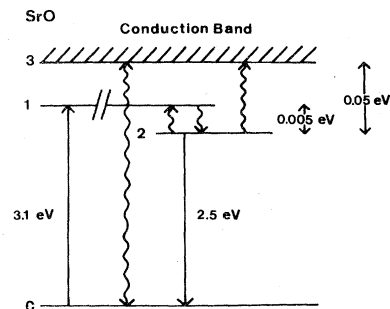


FIG. 7. Energy-level diagram for the F^+ center in SrO. Nonradiative transitions are shown as wavy lines and optical transitions as straight lines. Recent theoretical work (Ref. 6) suggests that the levels marked 1 and 2 are of mainly ${}^2T_{1u}$ and ${}^2A_{1g}^*$ character, respectively. The level labeled 0 is the ${}^2A_{1g}$ ground state.

Excitation into the F^+ band raises an electron from the ground state 0 to level 1. The center, then, relaxes and at the lowest temperatures radiative decay to the ground state occurs from level 2 with a rate constant K_{20} . Nonradiative transitions occur between levels 1 and 2, with a down rate of k_{12} and an up rate of k_{21} . Rates k_{13} and k_{23} represent thermal ionization into the conduction band from levels 1 and 2, respectively. In order to account for the decrease in fluorescence intensity between 10 and 50 K, the decay from level 1 to the ground state must be nonradiative and the rate for this process is represented by k_{10} . If the populations of levels 1 and 2 are n_1 and n_2 , respectively, and if the excitation rate is n_0W , the rate equations may be written:

$$\begin{aligned}\dot{n}_1 &= n_0W - n_1(k_{10} + k_{12} + k_{13}) + n_2k_{21} \\ \dot{n}_2 &= n_1k_{12} - n_2(K_{20} + k_{21} + k_{23}).\end{aligned}\quad (1)$$

Under steady-state conditions, \dot{n}_1 and \dot{n}_2 are zero and the quantum efficiency for fluorescence, η , can be written,

$$\eta = \frac{n_2K_{20}}{n_0W} = \frac{n_2K_{20}}{n_1(k_{10} + k_{12} + k_{13}) - n_2k_{21}}. \quad (2)$$

After some manipulation η may be written in the form

$$\eta = \frac{1}{1+A}, \quad (3)$$

with

$$A = \frac{k_{23}}{K_{20}} + \frac{(k_{10} + k_{12})(K_{20} + k_{21} + k_{23})}{K_{20}k_{12}}. \quad (4)$$

If we make the simplifying and reasonable approximation that $k_{12} > k_{10} > k_{13}$, that is, that a nonradiative transition between levels 1 and 2 is the fastest process, then we may write:

$$A(T) = K_1 \exp(-E_1/k_B T) + K_2 \exp(-E_2/k_B T), \quad (5)$$

where we have used

$$\begin{aligned}k_{23} &= k_{23}^0 \exp(-E_1/k_B T), \\ k_{21} &= k_{12} \exp(-E_2/k_B T),\end{aligned}\quad (6)$$

where E_1 is the difference in energy between level 2 and the conduction band and E_2 is the difference in energy between levels 1 and 2. In Eq. (5),

$$K_1 = k_{23}^0/K_{20} \quad (7)$$

and

$$K_2 = k_{10}/K_{20}.$$

It is worth noting that the quantum efficiency for a two level model⁹ has the same form as Eq. (3) ex-

cept that, in this case, $A(T)$ consists of single exponential. The effect of including an additional level is to introduce a second exponential into the formula and hence a second stage into the temperature dependence of the fluorescence decay.

The solid line in Fig. 4 is a fit of Eqs. (3) and (5) to the experimental data for the neutron-irradiated sample. From the fit we obtain $E_1 = 0.044$ eV and $E_2 = 0.004$ eV. A fit to the data obtained from the proton-irradiated sample gives similar values for the parameters and these are shown in Table I.

The two thermally activated processes which lead to a decrease in the quantum efficiency for fluorescence with increasing temperature (i.e., excitation from level 2 to level 1 followed by nonradiative decay to the ground state or thermal excitation into the conduction band) also should lead to a decrease in the fluorescence lifetime with the same temperature dependence. The continuous line in Fig. 6 is a fit of Eqs. (3) and (5) to the fluorescence lifetime data, from which we obtain $E_1 = 0.057$ eV and $E_2 = 0.007$ eV, values slightly larger than those found from the fluorescence intensity data. The model also predicts that only direct thermal excitation from level 2 to the conduction band will lead to photoconductivity, so that photoconductivity is expected to occur only during the second stage of fluorescence decay, that is, above 60 K. This behavior is actually observed.

The average value for E_2 is 0.005 eV. It is difficult to compare this number with the value estimated from the theoretical model. In the theoretical calculation the separation of the ${}^2A_{1g}^*$ and ${}^2T_{1u}^*$ state at the minimum of the ${}^2A_{1g}$ configuration coordinate curve was found to be 0.06 eV. However, when the Jahn-Teller energy was added, the ${}^2T_{1u}$ minimum in T_{2g} space became almost degenerate in energy with the ${}^2A_{1g}$ minimum in A_{1g} space. A value of 0.005 eV is therefore not unreasonable. The average value for E_1 was found to be 0.05 eV, which is to be compared with a value of 0.12 eV obtained from the photoconductivity measurements and a value of 0.2 eV obtained from the theoretical model. The reason for the discrepancy between

TABLE I. Energy separation between the A_{1g}^* state and the conduction band of the relaxed F^+ center in SrO, E_1 ; energy separation between the A_{1g}^* state and the lowest ${}^2T_{1u}$ state, E_2 . $K_1 = k_{23}^0/K_{20}$ and $K_2 = k_{10}/K_{20}$ are pre-exponential factors (see text).

Sample (method)	E_1 (eV)	E_2 (eV)	K_1	K_2
Proton-irradiated	0.049	0.004	362	0.554
Neutron-irradiated	0.044	0.004	407	0.950
Lifetime	0.057	0.007	579	1.260
Average	0.050	0.005	449	0.921

the value from the photoconductivity measurements and the fluorescence measurements is not clear. A value derived from photoconductivity data is generally less certain because of uncertainties in the temperature dependence of the mobility. However, this uncertainty would not be expected to account for the magnitude of the discrepancy. The photoconductivity measurements were made on samples containing a very small concentration of F^+ centers³ and it is possible that these were somehow influenced by impurities. At the moment we have no satisfactory explanation for the observed discrepancies in the values of E_1 .

The average value for $K_1 = k_{23}^0/K_{20}$ is 449. Since we know that K_{20} is about $2 \times 10^6 \text{ sec}^{-1}$, we can estimate that k_{23}^0 is about 10^9 sec^{-1} , which is quite acceptable for a preexponential factor. K_2 , on the other hand, is found to be approximately unity, which suggests that $k_{10} \sim 2 \times 10^6 \text{ sec}^{-1}$. This value seems slightly small but also suggests that thermal excitation from level 1 to level 3 is very unlikely, if our approximation that $k_{13} < k_{10}$ is correct.

It can be concluded, then, that a three level

model, which is in accord with recent theoretical work, is able to explain satisfactorily the temperature dependence of the F^+ fluorescence in SrO. The model does not explain, however, the mechanism by which thermally ionized electrons return to the ground state of the F^+ center. No long-lived phosphorescence has been detected thus far, but this has not been pursued in detail yet. The F^+ absorption band is not bleached, however, even at temperatures above 120 K, so that some efficient return path must be operative.

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