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Effect of Electric Field and Temperature on the Radiative Lifetime of the F Center[*][†]

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The lifetime of the excited F center at 4.2 °K and the changes in the radiative lifetime induced by an applied electric field and by increasing temperature have been measured in KCl, KF, and NaF with sufficient precision to test recent models for the relaxed excited states. The quantities measured were the luminescent decay time τ (using a pulse sampling technique), the relative luminescent yield η (using conventional techniques), and the emission-line-shape function. Changes in lifetime were measured for [100] applied dc fields of 0–140 kV/cm at 4.2 °K. These changes were of the form $\Delta\tau/\tau = -\beta F^2$, where F is the field in kV/cm, and β is $(5.8\pm0.5)\times10^{-6}$ in KCl, $(4.0\pm0.3)\times10^{-6}$ in KF, and $(3.0\pm0.3)\times10^{-6}$ in NaF. Lifetime and yield were measured from 4.2 to 150 °K with approximately 1% precision. In KCl and KF, these data are used to demonstrate that the only two decay modes from the relaxed excited states are emission and thermal ionization, so that the radiative lifetime is τ/η. In NaF, another decay mode during relaxation appears to complicate the results, but the radiative lifetime can be extracted using additional data reported by Podini. In all three cases, the radiative lifetime decreases as the temperature increases. Both the electric field and the temperature effects on the radiative lifetime are quantitatively consistent with the mixed-state model recently proposed by Bogan in which the lowest emitting state is presumed to be $2s$-like, with a large admixture of $2p$ states. Values for the characteristic parameters, the mixing parameter α, and the level separation $\langle\delta E\rangle$ are determined from these data and agree with values determined in a different manner by Bogan.

I. INTRODUCTION

The F center in alkali halides consists of an electron trapped at a single halogen vacancy. Its presence in a crystal is characterized by several broad optical-absorption bands in or near the visible spectrum. Excitation in any of these absorption bands, at sufficiently low temperatures, leads to a single broad emission band. Although the F center has been studied for many decades, it is only very recently that an understanding of the states responsible for this emission is emerging.[1]

Swank and Brown[2] were the first to measure the decay time of the F-center luminescence. They found that the radiative lifetime of the excited center (F^*) was approximately two orders of magnitude longer than the value to be expected from the oscillator strength in absorption. Of the various explanations which they proposed for this discrepancy, the diffuse p-state model gained wide acceptance as a result of the work of Fowler.[3] He was able to show that the Γ_4^- ($2p$-like) state of F^* would become more diffuse as the surrounding ions adjusted to the change in charge distribution following the optical excitation. This would reduce the matrix element for emission to the ground state. Using plausible values for an effective dielectric constant in a semicontinuum model, he was able to predict the right order of magnitude of the decay time.

However, the recent work of Bogan[4] and of Kühnert[5] could not be explained by the diffuse p-state model. Both these authors studied the Stark effect on the relaxed excited state of the F center by analyzing the electric-field-induced linear polarization of the luminescence. Their results implied that the luminescent state of F^* has a considerable amount of $2s$ character. Whether the relaxed excited state consisted of completely degenerate $2s$-$2p$ states, as assumed by Kühnert, or of strongly mixed but not degenerate states, as assumed by Bogan, could not be ascertained from the polarization measurements alone. Such information can be obtained, as is shown in Sec. II, from precise lifetime measurements.

The present paper reports a study of the variation of the radiative lifetime of F^* with temperature and electric field in KCl, KF, and NaF, using a sampling technique to determine decay time and quantum efficiency of the F-center luminescence to considerably better precision than previously obtained. Our results strongly support Bogan's model for the luminescent states of the F center in alkali halides.

II. THEORY

A. Bogan's Model

We shall now summarize the essential features of the model for the relaxed excited states of the F center as proposed by Bogan.[4]

The basic assumption of the model is that the $2s$ state plays a role at least as important as the $2p$ state in the emission process.

Serious consideration had not been given previously to the $2s$ state even after the measurement of Chiarotti *et al.*[6] which indicated that, in absorption, the $2s$ state lay only 0.1 eV above the $2p$ state. This lack of consideration probably can be attributed to the simplicity of the model proposed by Fowler, which only involved a spatial expansion of the $2p$ wave function with no change in its electronic character due to the interaction with the lattice. Since Fowler's model appeared to be consistent with the measurements devised to test it, the introduction of a complicating feature such as an interaction between the $2p$ and $2s$ states seemed unnecessary. Only recently, stimulated by the work of Bogan and of Kühnert, have some calculations been made which involve the $2s$ state. Both Fowler *et al.*[7] and Wood and Öpik[8] have found that after relaxation the $2s$ and $2p$ states may be very close together. For KCl, Wood and Öpik found that the $2s$ state crosses the $2p$ state and ends up ~0.08 eV lower in energy.

These calculations are certainly consistent with Bogan's assumption that F^* states consist of nearly degenerate strongly mixed $2s$ and $2p$ states, with the predominantly $2s$ state lower in energy. Although neither Fowler *et al.* nor Wood and Öpik actually considered $2s$-$2p$ mixing in their calculation, it is almost inevitable that such mixing should occur if the levels are very close in energy.

The exact nature of the mixing is not easy to ascertain from simple considerations. Since no quantitative theory of this strongly coupled electron-lattice problem was available, Bogan explained the mixing in terms of a semiclassical model which assumed that the electrons would respond adiabatically to the fluctuating internal electric fields due to odd-parity LO phonons. Therefore the mixing was interpreted as an internal Stark effect.

Assuming that the main contribution to the mixing is given by optical phonons of Γ_4^- symmetry, then first-order perturbation theory yields for the "mixed" states

$$|2s'\rangle = (1+\alpha^2)^{-1/2}(|2s\rangle + \alpha|2p_x\rangle) \ ,$$
$$|2p_x'\rangle = (1+\alpha^2)^{-1/2}(|2p_x\rangle - \alpha|2s\rangle) \qquad (1)$$

for a distortion in the x direction. The "perpendicular" states $|2p_z\rangle$, $|2p_y\rangle$ are not affected by the distortion in the x direction and remain degenerate. Energetically, the $|2s'\rangle$ state is lowest. An energy δE above it is the degenerate pair $|2p_z\rangle$ and $|2p_y\rangle$ and above these is the $|2p_x'\rangle$ state.

At low temperature, the F emission will originate only from the $|2s'\rangle$ state. Its radiative lifetime τ_s' will depend on the mixing coefficient α:

$$\frac{1}{\tau_s'} \propto \sum_j |\langle 1s\, |x_j|\, 2s'\rangle|^2 = \frac{\alpha^2}{1+\alpha^2} M^2 \ , \qquad (2)$$

where $M^2 = |\langle 1s\,|x|\,2p_x\rangle|^2$. This equation clearly shows that an essential reason for the long lifetime of the F^* could be due to the predominantly $2s$-like character of the emitting state. This by no means excludes the possibility that the state is also diffuse. The calculations of Fowler *et al.* and of Wood and Öpik already mentioned, and also of Bogan,[4] indicate that all the excited states of F^* should be quite diffuse after relaxation.

B. Field and Temperature Dependence of Radiative Lifetime

1. *Field Dependence*

If an external electric field is applied – say, in the z direction – a mixing of $|2p_z\rangle$ state into the $|2s'\rangle$ state will take place. Assuming that this additional mixing $\Delta\alpha$ is small compared to the mixing due to internal fields, first-order perturbation theory can be applied to calculate the resulting change in radiative lifetime. This change when averaged over all distortions will be a decrease given by

$$\frac{\Delta\tau_s'}{\tau_s'} \simeq -\frac{\Delta(1/\tau_s')}{1/\tau_s'} = -\frac{(\Delta\alpha)^2}{\alpha^2(1+\alpha^2)} . \qquad (3)$$

Since $\Delta\alpha$ is proportional to the applied field, this result then predicts a quadratic decrease of the radiative lifetime with applied electric field. It should be noted that Kühnert's assumption that the $|2s\rangle$ and $|2p\rangle$ states are initially degenerate implies that no field dependence of the radiative lifetime should be observed. In this sense a precise lifetime measurement is crucial to distinguish between Kühnert's and Bogan's models.

The additional mixing also induces a linear polarization in the emission, since it enhances the emission polarized parallel to the field at the expense of the emission polarized perpendicular to the field. Since the basic mechanisms for the the change in lifetime and for the induced polarization are the same, they must be related. In fact, the polarization P is given by[4]

$$P=\tfrac{3}{2}(\Delta\alpha/\alpha)^2, \tag{4}$$

and therefore

$$\Delta\tau/\tau=\tfrac{2}{3}(1+\alpha^2)^{-1}P. \tag{5}$$

This relationship allows an estimation of the size of the relative change in lifetime. Using the data reported by Bogan[4] for the polarization and α, the model predicts a relative decrease in lifetime of ~6% for a field of 100 kV/cm in KCl.

2. *Temperature Dependence*

In studying the temperature dependence of the lifetime on the basis of Bogan's model, it must be kept in mind that this is only a very simple model. A temperature increase may have many effects on the system, some of which are easily accounted for, while others are more difficult to investigate. The importance of the complicating effects will increase as the temperature is increased. On the other hand, one effect is expected to dominate all others at low temperature (say, below 100 °K) and that is the effect of the emission from the higher-lying states becoming more pronounced with increasing temperature. Since the F^* decay has been found to be a single exponential, all the levels involved in the emission must be in equilibrium, so they should be populated according to Boltzmann statistics. Since the transition probability from the higher-lying states is greater, the increase in emission from these states will result in a decrease in radiative lifetime as the temperature increases.

Assuming for simplicity that the higher-lying states are degenerate, we obtain for the temperature variation of the lifetime

$$\frac{\tau(T)}{(0)}=\frac{1+3e^{-\langle\delta E\rangle/kT}}{1+3Re^{-\langle\delta E\rangle/kT}}, \tag{6}$$

where $R=(1+\tfrac{2}{3}\alpha^2)/\alpha^2$ is the ratio of the $|2s'\rangle$ and $|2p'\rangle$ lifetimes, and $\langle\delta E\rangle$ is the time average of the energy separation between $|2s'\rangle$ and the other states.

Another effect which is expected to be important even at low temperature is the increase in the mixing parameter α due to the increased population of optical phonons responsible for the internal Stark fields. In a somewhat arbitrary fashion we neglect this effect, since Bogan's results and ours indicate that the mixing parameter α is already large, so that the additional mixing due to temperature would not have a very large effect.

III. RELATION OF MODEL PARAMETERS TO OBSERVABLES

A. Decay Modes of F^*

Bogan's model is concerned with the behavior of the radiative lifetime of F^*, whereas what is measured experimentally is the decay time τ. This decay time is determined not only by the radiative transition to the ground state but also by other nonradiative transitions which depopulate F^*.

The original model proposed by Swank and Brown[2] assumed that all the excited F centers decay through the lowest relaxed state, whose lifetime determines the decay time of the emission. Furthermore, they postulated that only two decay channels were available: radiative emission and thermal ionization. Thus, they expressed the F^* decay probability as

$$1/\tau=1/\tau_r+(1/\tau_0)e^{-\Delta E/kT}, \tag{7}$$

where τ is the observed lifetime, $1/\tau_0$ is the ionization attempt frequency, and ΔE is the activation energy for ionization. The lifetime τ is related to the radiative lifetime τ_r by

$$\eta_r=\tau/\tau_r, \tag{8}$$

where η_r is the fluorescent yield from the relaxed excited state.

These expressions were satisfactorily tested by their measurements of fluorescent and photoconductive decay times and yields for four alkali halides.

More recent studies, however, have shown that the decay can be more complicated for some other F centers. In NaF, for instance, Podini[9] found a third nonradiative nonphotoconductive decay mode. Moreover, in studies of electric field effects on the F-center emission several workers[4,10,11] have observed that ionization may occur during relaxation. This means that in general η_r will not be a readily measurable quantity. What can be measured is the quantum efficiency η_e defined by

$$\eta_e=\frac{\text{number of photons emitted}}{\text{number of photons absorbed}}. \tag{9}$$

It is customary to assume that η_r is proportional to η_e. If there is a channel available for the excited electron to escape or to tunnel to the ground state, this assumption cannot be made. If such channels are present, in general, they could be field or temperature dependent. So, if η_0 is defined as the probability for an excited F electron to reach the relaxed excited state, then

$$\eta_e = \eta_0 \eta_r \ . \tag{10}$$

This means that in order to obtain a value for τ_r from lifetime and quantum yield measurement, care must be taken to see whether or not $\eta_0 = 1$.

B. Correction for Emission Energy Dependence

The transition probability is not only proportional to the transition dipole moment, but also to the cube of the emission energy. This fact will introduce an extra field and temperature dependence of the lifetime due to the shift or temperature change. These effects must then be taken into account in order to isolate the field and temperature effect on the transition probability predicted by Bogan's model. The proper way to include such a correction depends on assumptions about how the levels shift or mix. We will take the change in the cube of the experimentally determined emission energy E, averaged over the whole emission band, as a rough measure of how such changes affect the radiative lifetime.

IV. EXPERIMENTAL PROCEDURES

A. Lifetime Measurements

The time decay of F-center luminescence was measured using pulsed excitation and a sampling technique. The pulsed lamp was a TRW Nanosecond Spectral Source, i.e., a nitrogen discharge operating at a repetition rate of ~2 kHz with a peak power of 140 W, a duration of ~20 nsec, and a relatively sharp cutoff, but with a weak long-lived tail.

The F-emission pulse was detected with a cooled RCA 7102 photomultiplier, whose output pulse was amplified and fed into the homemade sampling system shown in Fig. 1. The variable delay was scanned over the range 0–10 μsec and the stretched output of the delayed gate (typically 10 nsec wide) was synchronously detected and recorded to show the time decay of the emitted intensity. The rise time of the whole system was ~7 nsec.

The measured time decays were affected by the finite decay time of the excitation pulse. The characteristic F-center decay time was determined by convoluting the measured pulse shape $f(t)$ with a single exponential decay function $g(t) = g_0 e^{-t/\tau}$ and comparing with the observed decay $I(t)$, i.e.,

$$I(t) = \int_0^t f(t')\, g(t-t')\, dt' . \tag{11}$$

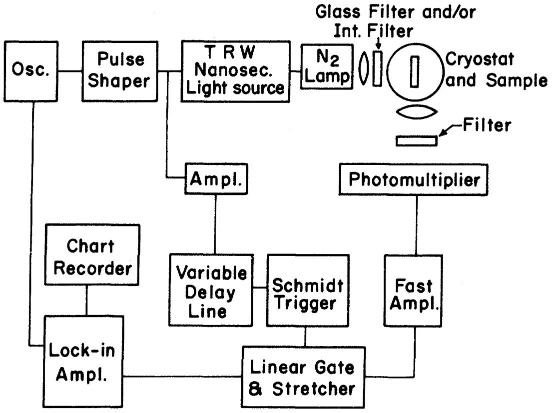

FIG. 1. Schematic diagram of pulse-sampling system.

The major assumption in this analysis is that $g(t)$ is of the form $g_0 e^{-t/\tau}$. The best evidence supporting this assumption is the recent work of Bertolaccini *et al.*[12] on the F-center decay in KCl, using a photon sampling system. Because this system was more sensitive than the present system, these workers could use a pulsed lamp especially selected to have considerably smaller long-lived components. They found no deviation from a single exponential decay over four orders of magnitude in intensity. Our results are consistent with this result, but are by no means as definite.

B. Yield Measurements

The relative luminescent yield as a function of field and temperature was determined using both pulsed and dc excitation. For pulsed excitation, the gate was left open throughout the emission pulse and the same synchronous detection system was used. For dc excitation a tungsten lamp and filters and monochromators were used in the conventional fashion but with extra care and the minimum light level possible. Samples were chosen to give total absorption, and the emission data were corrected for the spectral response of the detection system. Yield data were normalized to the yield at 4.2 °K and zero field.

C. Band Shape

In order to correct for the effect of band shift and broadening in the emission, the band shape was measured as a function of temperature using standard procedures with dc excitation.

D. Samples

KCl and NaF samples were obtained from the Harshaw Chemical Co. and were also grown by the Kyropoulos technique in the Crystal Growing Facility at Cornell University. No noticeable difference in behavior was observed for samples obtained from the latter source.

Most samples were colored by x irradiation at liquid-nitrogen temperature, after which the sample was warmed in the dark, transferred promptly to the experimental cryostat under safelight, and cooled to liquid-nitrogen temperature again. All samples were checked to ensure that no *M*-center emission was present.

E. Temperature Control

For temperature-dependence measurements, the sample was mounted in a conduction cryostat on a holder with a small resistance heater and exchange-gas heat switch which permitted the temperature to be controlled to within about $\frac{1}{2}$ °K over the range 14–160 °K. The actual sample temperature was monitored with thermocouples and carbon resistors.

F. Electric Fields

To determine field-induced changes, a dc field was applied while the sample was immersed in liquid helium at 4.2 °K. The sample, typically 20 × 20 × 1 mm, was sandwiched between electrodes, one blocking and the other a partially transparent (100 wires/in.) mesh screen. Only the part of the sample near the center of the electrodes was colored with x rays.

The sample was usually excited through the edge of the sample and the emission observed through the mesh electrode. This results in the observation of light polarized only perpendicular to the applied field. It was also necessary to measure the lifetime for light polarized parallel to the applied field. For this measurement, the crystal was excited through the mesh electrode and the emission observed through the edge of the sample with a Rochon prism to eliminate the perpendicular component of the light. The dc voltages applied were typically 0–25 kV. The highest field strength used was 135 kV/cm in most cases.

Further details of the experiment are given in Ref. 13.

V. EXPERIMENTAL RESULTS

A. Temperature Dependence

1. *Band Shape*

The first task was to determine that the observed emission at all temperatures was due to the *F* center and only the *F* center. This was verified by measuring the emission band shape carefully at several temperatures from 4.2 to 150 °K.

The emission spectra for KCl agreed very well with those reported previously by Gebhardt and Kühnert.[14] For KF and NaF, temperature-dependence data are not available in the literature. The low-temperature spectrum for KF has the same peak position and half-width as those reported by Bosi *et al.*[15] The *F*-emission band in NaF is overlapped by a second emission band located at ~1.03 μ which was also observed by Bosi. Emission spectra for NaF at two temperatures are shown in Fig. 2. The intensity of the second band appeared to be somewhat sample dependent, but nearly independent of temperature. It was presumed to be extrinsic to the *F* center (probably the F_2^+ center) and was subtracted from all data.

The emission-band-shape function (emission intensity per unit energy bandwidth divided by photon energy cubed) was determined as a function of temperature in KF and NaF, as well as in KCl. The half-width and peak position of the shape function were fitted by the expressions

$$H(T) = H(0)\ \coth^{1/2}(\hbar\omega/2kT) \tag{12}$$

and

$$E(T) = E(0) + B[1 - \coth(\hbar\omega/2kT)], \tag{13}$$

where $E(T)$ is the energy of the peak position of the emission-shape function, and $H(T)$ is the full width at half-maximum at temperature T. The values obtained for the parameters are listed in Table I.

2. *Lifetime*

Low temperature. The values of the lifetime at 4.2 °K are reported in Table II. These values represent averages for several scans per sample, and several samples per alkali halide. The error estimate is based mainly on scatter of these re-

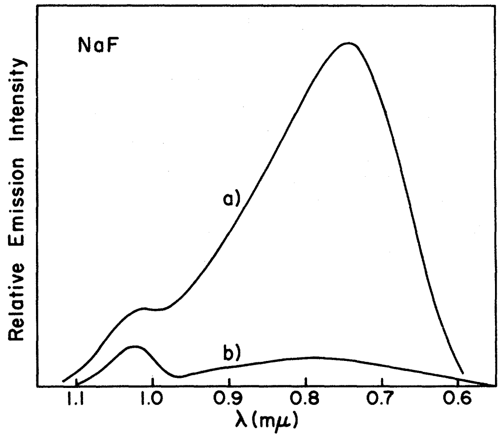

FIG. 2. NaF emission spectra at (a) 17 and (b) 180 °K for excitation at 350 nm.

TABLE I. Temperature-dependence parameters (in eV).

	KF	NaF
$H(0)$	0.39	0.50
$E(0)$	1.63	1.65
B	0.7	0.6
$\hbar\omega$	0.037	0.032

sults.

The lifetime was found to be unchanged when the intensity of the pumping light was varied by an order of magnitude. The value obtained for the lifetime in KCl at 77 °K is 620 ± 15 nsec, in agreement with the value 628 ± 7 nsec reported recently by Bertolaccini *et al.*[12] The intensity of the excitation which they employed was several orders of magnitude lower than that used here.

Since the concentration independence of the lifetime was established by Bertolaccini *et al.*, this test was not repeated here. In addition, their experiments were performed with additively colored KCl, while x-ray coloration was used here. A control experiment was performed using an additively colored KCl sample but no observable difference was found. A sample of KF was also irradiated with electrons at liquid-nitrogen temperature (LNT). This sample exhibited the same characteristics as the x-rayed samples. Thus, the lifetime seems to be a well-defined quantity, independent of sample source and sample preparation.

Temperature dependence. The temperature dependence of the lifetime in KCl, KF, and NaF is shown in Fig. 3. The data represent several runs on two or more samples in each case. The scatter in the results is less than 1% of the low-temperature value.

3. *Quantum Efficiency* η_e

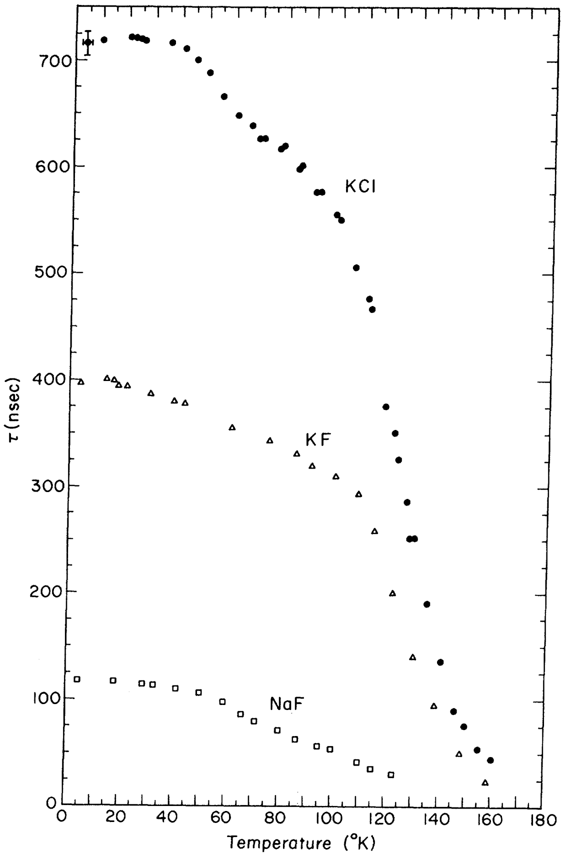

FIG. 3. Measured decay time for F-center luminescence versus temperature.

TABLE II. Low-temperature lifetimes (in nsec).

Crystal	τ(4.2 °K)
KCl	717 ± 15
KF	380 ± 20
NaF	117 ± 5

The relative yield $\eta_e(T)/\eta_e(0)$ $(=\eta_e')$ as a function of temperature is shown for the three alkali halides in Fig. 4. Each plot represents one run, with the exception of the KCl plot, which has the results of both pulsed and dc excitation. η_e' for KF and NaF was determined solely by dc excitation. Several scans were taken in each alkali halide. They showed consistency with these results. These were the best runs, in which the minimum excitation light level could be used, in which the drift during the run was minimal, and in which the temperature control functioned well. The pulsed and dc excitation data for KCl show extremely good agreement up to approximately 140 °K.

B. Electric Field Dependence

1. *Lifetime*

The field-induced changes in lifetime were measured differentially from 0 to approximately 135 kV/cm at 4.2 °K and are shown in Fig. 5. The lifetime decreases quadratically with applied field in all three alkali halides. The change is the same for emission polarized perpendicular and parallel to the applied field in the cases where both could be measured. The data correspond to several different runs for each alkali halide. Both x-ray and electron-irradiated samples of KF were used in

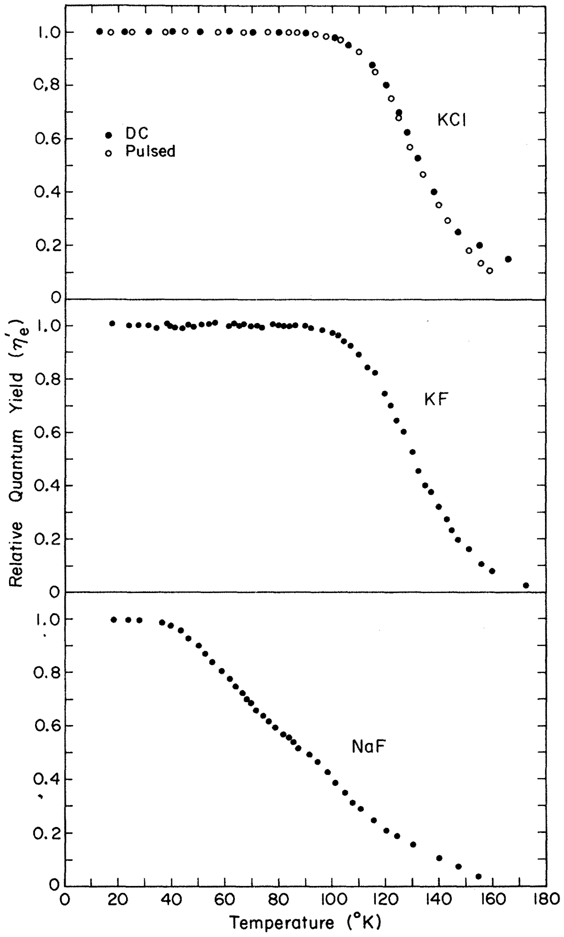

FIG. 4. Relative luminscent yield versus temperature.

these experiments, with no noticeable difference in behavior between these samples.

2. *Quantum Efficiency*

The effect of field on the quantum yield was not measured for KCl, since this had been measured previously by Kühnert[5] and by Bogan,[4] and since K-band excitation was used here. Bogan found that K-band excitation leads to an extra field-induced quenching compared to F-band excitation, presumably as a result of ionization during relaxation. Hence it would not affect the radiative lifetime of the relaxed state, but would make the yield data useless.

For KF, where the excitation occurred in the F band, any field-induced change in integrated intensity of the pulse was less than 1%. This agrees with Bogan's finding of no change in yield for his highest field of 50 kV/cm.

For NaF, there is a field-induced decrease in yield even for F-band excitation, as noted by Bogan. We have measured the changes in $I_\parallel$ and $I_\perp$ separately as shown in Fig. 6. The polarization

$$P \approx \frac{1}{2}\left(\frac{\Delta I_\parallel}{I_\parallel} - \frac{\Delta I_\perp}{I_\perp}\right) = (3.2 \pm 0.3) \times 10^{-6} F^2 \qquad (14)$$

and the change in yield

$$\Delta\eta \approx \frac{1}{3}\left(\frac{\Delta I_\parallel}{I_\parallel} + \frac{2\Delta I_\perp}{I_\perp}\right) = -(4.6 \pm 0.3) \times 10^{-6} F^2 \qquad (15)$$

(where F is in kV/cm) obtained with this pulsed method are in reasonable agreement with the results of Bogan's modulation experiment.

VI. ANALYSIS

The raw results on the field and temperature dependence of the F-center decay times presented in Sec. V appear to be in qualitative agreement with the predictions of the mixed-state model. However, the model is concerned with the radiative lifetime and radiative transition matrix elements, and a crucial part of the analysis is determining these quantities from the measured data.

A. KCl

The first and most difficult question is to determine the radiative lifetime. As discussed earlier, the radiative lifetime is $\tau_r = \tau/\eta_r$, where η_r is the branching ratio for emission from the

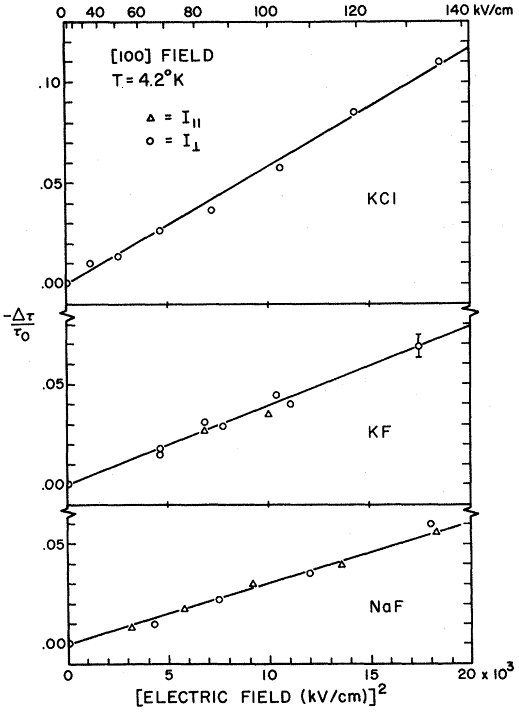

FIG. 5. Fractional decrease in luminescent decay time versus the square of the applied dc field.

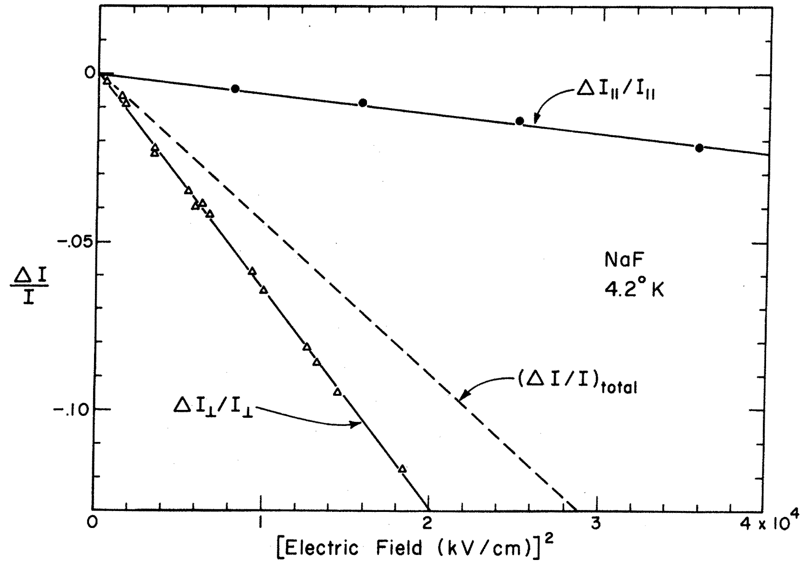

FIG. 6. Fractional change in F-center emission intensity versus the square of the applied dc field in NaF.

relaxed excited state. But the measured quantities were τ and η_e', the relative quantum yield for emission. The latter can be affected by other nonradiative decay modes, particularly by ionization occurring during relaxation.

One test of whether other decay modes are present is to compare the temperature-dependence data with the simple two-channel model of Sec. III. From Eq. (7), the probability of nonradiative decay in this model is

$$(1-\eta_r)/\tau = 1/\tau_0\, e^{-\Delta E/kT}. \qquad (16)$$

Figure 7 shows a plot of $\ln(1-\eta_e')/\tau$ versus $1/T$. The KCl data are fitted very well over three decades by Eq. (16), if we assume $\eta_r = \eta_e'$. The parameters for the straight line in the figure are $\Delta E = 0.142$ eV and $1/\tau_0 = 1.0 \times 10^{12}$ sec^{-1}. These values are in good agreement with Swank and Brown's results for the photoconductivity, implying that thermal ionization from the relaxed state is the only nonradiative decay mode for the excited F center. Hence, we can assume that $\eta_r = \eta_e'$, so that $\tau_r = \tau/\eta_e'$. A plot of $\tau(T)/\eta_e'(T)$ is shown in Fig. 8.

The expression for the radiative lifetime involves a factor of $1/E^3$ as discussed in Sec. III. Using the band shift and broadening data to calculate $\langle E^3(T)\rangle$, this contribution to the temperature dependence can be eliminated by multiplying $\tau_r(T)$ by $\langle E^3(T)\rangle / \langle E^3(0)\rangle$. This corrected value is also plotted in Fig. 8.

The field-induced changes in radiative lifetime are somewhat more difficult to infer.

As mentioned earlier, η_e' is known to be constant with electric field in KCl up to about 100 kV/cm for excitation in the F band at temperatures below about 20 °K. [5,16] Above this field value the yield decreases by perhaps 4% up to our highest field value of 135 kV/cm. The yield also decreases if K-band excitation is used in the presence of a field.

The latter result implies that some ionization occurs *during* relaxation for K-band excitation, but not for F-band excitation, at least up to 100 kV/cm. Although the F center in KCl was excited with K-band light for these experiments and some

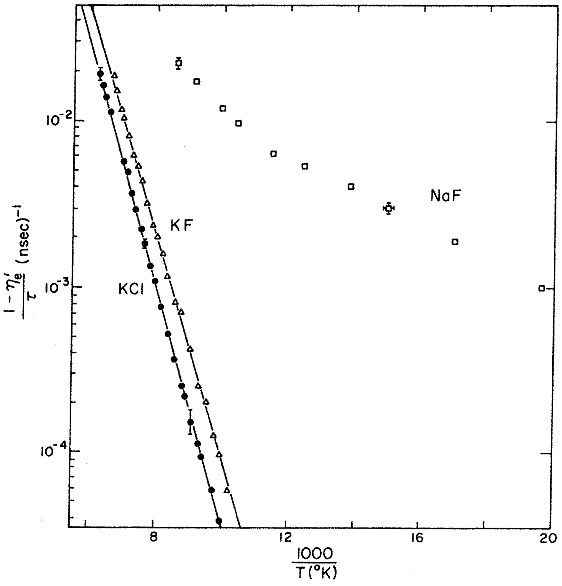

FIG. 7. Temperature dependence of the nonradiative decay probability of the excited F center.

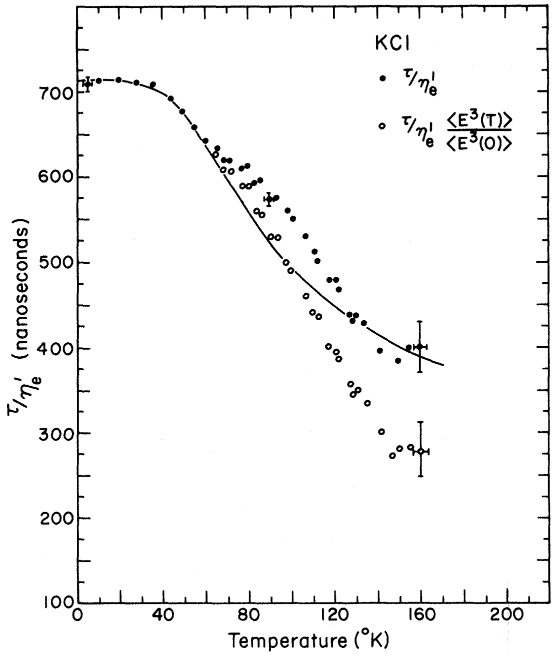

FIG. 8. Temperature dependence of the radiative lifetime in KCl. The solid line indicates the best fit to the data using Eq. (24) and the parameters given in the text.

quenching may occur, it is still true that the branching ratio η_r in the relaxed state must be independent of field, since η_e' is constant for excitation in the F band. So it is reasonable to assume that η_r is constant below 100 kV/cm at 4.2 °K.

For fields above 100 kV/cm, it is not certain whether the loss of yield is a result of ionization during or after relaxation. In the former case, η_r cannot be equated to η_e'. Until a measurement of the time dependence of the nonradiative channel at high fields is made, the choice is not clear. However, we prefer to assume that the field-induced loss occurs during relaxation, since the K-band data show that this sort of process is reasonable. We then assume that $\eta_r = 1$ for all fields measured. Thus, we have taken $\Delta\tau_r/\tau_r = \Delta\tau/\tau$.

As before, the lifetime must be modified by $\langle E^3\rangle$ to isolate the effect of the electric field on the radiation dipole matrix element. Since the band shifts to the red and is slightly broadened with applied electric field, there is a net decrease of this term. For small changes,

$$\frac{\Delta\langle E^3\rangle}{\langle E^3\rangle} \simeq \frac{3\left[\,(2\,\Delta\sigma/\sigma + \Delta E_p/E_p\,)\,\sigma^2/E_p^2 + \Delta E_p/E_p\,\right]}{3\,\sigma^2/E_p^2 + 1}\,, \qquad (17)$$

where 1.4σ is the half-width and E_p is the peak energy of the shape function. ΔE_p and $\Delta\sigma$ depend quadratically on the applied field. Hence the $\langle E^3\rangle$ factor is also, to first approximation, dependent on the square of the field. Therefore, this correction only has the effect of making the coefficient of the lifetime dependence on electric field more negative. If $M^2 = 1/\tau_r\langle E^3\rangle$, then

$$\Delta M^2/M^2 = (6.0 \pm 1.0)\times 10^{-6} F^2\,,$$

where F is in kV/cm for KCl.

B. KF

With the analysis in KCl in mind, a plot of $\ln[(1-\eta_e')/\tau]$ versus $1/T$ is also shown for KF in Fig. 7. It is seen that $(1-\eta_e')/\tau$ can be described extremely well by the expression $(1/\tau_0)\,e^{-\Delta E/kT}$, where $1/\tau_0 = 5\times 10^{11}$ sec^{-1} and $\Delta E = 0.135$ eV. This suggests that there is only one significant nonradiative channel, and that this is probably thermal ionization. Thus we make the same identification as before: $\eta_r = \eta_e'$.

A plot of $\tau(T)/\eta_e'(T)$ is presented in Fig. 9. Also plotted here are the corrected values

$$[\tau(T)/\eta_e'(T)]\langle E^3(T)\rangle/\langle E^3(0)\rangle.$$

As with KCl, the result clearly shows that the radiation dipole matrix element is increasing with temperature.

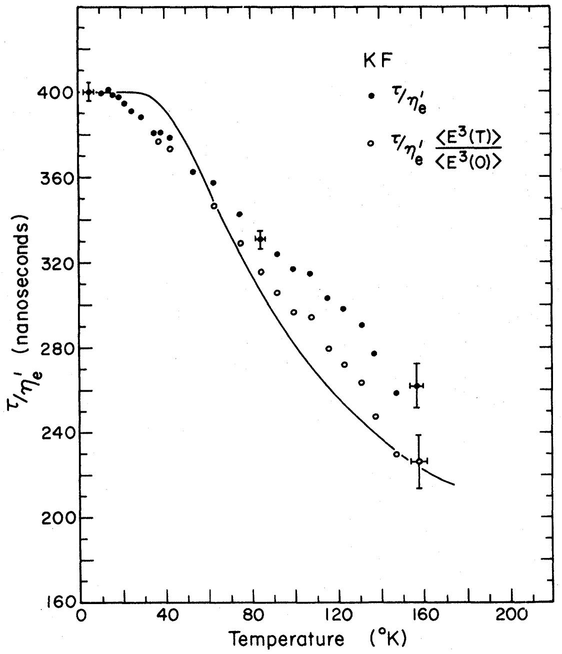

FIG. 9. Temperature dependence of the radiative lifetime in KF.

We make the same assumptions for the field dependence as for KCl. Bogan found that at approximately 18 °K, η_e' is constant with applied electric field up to the highest fields he attained (50 kV/cm). Although we did not measure the yield explicitly in KF, an estimated upper limit for the change of η_e' can be placed at – 1% at 140 kV/cm. This is based on estimates of the integrated intensity of the emitted pulse for the two polarizations. For these reasons, η_r is assumed to be constant in field over the entire range of fields attained and $\Delta\tau_r/\tau_r = \Delta\tau/\tau$.

The $\langle E^3\rangle$ correction is applied as before. This results in

$$\Delta M^2/M^2 = (4.2 \pm 0.6)\times 10^{-6} F^2, \tag{18}$$

where F is in kV/cm.

C. NaF

The data for NaF do not fall on a straight line in Fig. 7. This implies that the simple two-channel model does not apply, or that $\eta_r \neq \eta_e'$.

Podini[9] first noted this abnormal behavior. He found that $(1-\eta_e')/\tau$ did not correspond to the probability of photoconductivity, and that η_e' decreased before photoconductivity began. Podini found that the ratio of the relative photoconductive yield to the relative luminescent yield was of the expected form,

$$\frac{\eta_I'}{\eta_e'} = \frac{1/\tau_0 e^{-\Delta E/kT}}{1/\tau_r} = \frac{\tau_r}{\tau_0} e^{-\Delta E/kT}, \tag{19}$$

with $\Delta E = 0.12$ eV.

Tomura[17] and Honda observed the same anomalous behavior of η_e'. Both proposed another direct nonradiative channel from the relaxed excited state to the ground state to explain this behavior. An alternative hypothesis for NaF, which we prefer, is that there is some nonradiative decay mode before or during relaxation, but only the usual two channels after relaxation.

If we were to assume otherwise (that $\eta_r = \eta_e'$), we would find the surprising result that the radiative lifetime increases with increasing temperature. On the other hand, our alternative takes $\eta_r \neq \eta_e'$, and instead determines η_r from Podini's data as

$$\eta_r = \frac{1}{1+(\tau_r/\tau_0)e^{-\Delta E/kT}} = \frac{1}{1+\eta_I'/\eta_e'} . \tag{20}$$

Using this expression for η_r, we get $\tau_r = \tau/\eta_r$ as shown in Fig. 10. This result is much closer to the behavior of KCl and KF. The $\langle E^3\rangle$ correction is also plotted in the figure.

The field dependence also depends critically on which hypothesis we choose. If we assume that the field-induced quenching observed for NaF occurs from the relaxed excited state, then the field-induced change in radiative lifetime would be

$$\frac{d\tau_r}{dF} \simeq \frac{d(\tau/\eta_e')}{dF} = \frac{1}{\eta}\frac{\partial\tau}{\partial F} - \frac{\tau}{\eta^2}\frac{\partial\eta}{\partial F} . \tag{21}$$

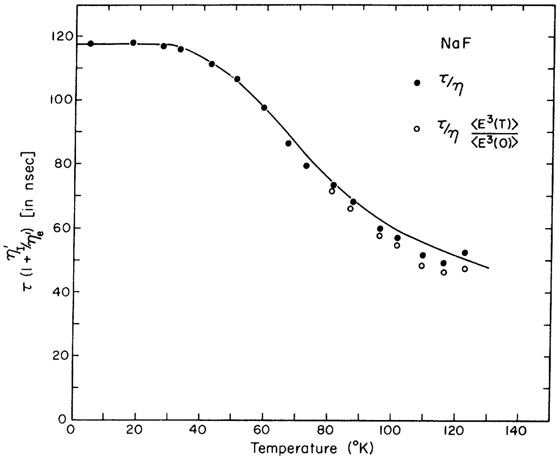

FIG. 10. Temperature dependence of the radiative lifetime in NaF.

Since the second term is larger than the first and of opposite sign, the net change would be an increase in radiative lifetime with field.

If we assume that the quenching in NaF occurs during relaxation for both F- and K-band excitation, then it is reasonable to presume that η_r is unaffected by field, just as for KCl and KF. In this case, $\Delta\tau_r/\tau_r = \Delta\tau/\tau$. Including the $\langle E^3\rangle$ correction, we get

$$\Delta M^2/M^2 = (3.0 \pm 0.5)\times 10^{-6} F^2, \tag{22}$$

where F is in kV/cm.

Clearly, the analysis of NaF is uncertain until this extra decay mode can be eliminated or better understood. We defer further comment about it until the next section.

VII. INTERPRETATION

A. Comparison with Mixed-State Model

The lifetime results reported in the preceding sections are in qualitative agreement with the predictions of Bogan's mixed-state model. In this section, a quantitative comparison with this model is made, and the significance of the parameters discussed.

There are two key parameters in the model: the mixing coefficient α and the energy level separation $\langle\delta E\rangle$, Bogan determined both of these from the temperature dependence of the field-induced polarization. However, these data were not very precise and the fit was not particularly good, so that his estimates for these parameters had a large uncertainty.

The parameters can also be determined in an independent way using our results on the lifetime. First, the mixing coefficient α can be determined from Eq. (5), which relates the change in radiative lifetime and the polarization at low temperatures. Within the framework of Bogan's model, this equation is not strictly correct. Instead, it should be rewritten as

$$\Delta M^2/M^2 = \tfrac{2}{3}(1+\alpha^2)^{-1} P(0) \quad . \tag{23}$$

That is, the effect of the $\langle E^3 \rangle$ factor on the radiative lifetime must be considered. A value for α^2 can be obtained using the values for $\Delta M^2/M^2$ and $P(0)$ reported in Table III.

The level separation $\langle \delta E \rangle$ can be determined by fitting the temperature dependence on the lifetime with Eq. (6). Again, this really describes the temperature dependence of the effective dipole matrix element, so

$$\frac{M^2(T)}{M^2(0)} = \frac{1+3Re^{-\langle \delta E \rangle/kT}}{1+3e^{-\langle \delta E \rangle/kT}} \quad , \tag{24}$$

where

$$R = \tfrac{2}{3} + 1/\alpha^2 . \tag{25}$$

1. *Potassium Chloride*

The value of α^2 determined for KCl from Eq. (5) is

$$\alpha^2 = 0.1\,^{+0.4}_{-0.1} \quad . \tag{26}$$

The relatively large uncertainty is due primarily to the large uncertainty in Bogan's measurement of $P(0)$. Kühnert measured $P(0)$ for KCl more precisely, using larger dc fields. If his value is used, then

$$\alpha^2 = 0.46 \pm 0.2 . \tag{27}$$

Restricting R to the range determined by these values of α^2, the best fit to the temperature-dependence data is that shown by the solid line in Fig. 8. This corresponds to $\alpha^2 \approx 0.5$ ($R = 2.75$) and $\langle \delta E \rangle = 0.018$ eV. The fit to the data is remarkably good up to 100 °K, but above this there is some discrepancy. No choice of parameters is able to give a close fit over the whole temperature range.

TABLE III. Field-induced changes [$\times 10^6$ (kV/cm)^2].

Crystal	$\Delta M^2/M^2$	$P(0)$
KCl	6.0 ± 1.0	10 ± 3[a] 13 [b]
KF	4.2 ± 0.6	8 ± 3[a]
NaF	3.0 ± 0.5	4 ± 1[a]

[a] Bogan (Ref. 4).

[b] Kühnert (Ref. 5).

2. *Potassium Fluoride*

The value of α^2 determined with Bogan's $P(0)$ is

$$\alpha^2 = 0.26\,^{+0.35}_{-0.20} \quad . \tag{28}$$

In this case, it is not possible to get such a close fit to the temperature-dependence data. However, a reasonable fit for this extremely simple model is obtained using a value of $\langle \delta E \rangle$ close to that found by Bogan, as shown in Fig. 9. The solid line is for $\alpha^2 \simeq 0.5$ ($R = 2.75$) and $\langle \delta E \rangle = 0.017$ eV. The discrepancies at low and intermediate temperatures are slightly larger than the experimental uncertainty.

3. *Sodium Fluoride*

For NaF, there is some uncertainty as to how to proceed because of the different behavior of the quantum efficiency η_e'. If one assumes as before that $\tau_r = \tau/\eta_e'$, then the radiative lifetime increases rather than decreases as the temperature is raised. This would imply that the lowest emitting state is predominantly $2p$-like. However, this conclusion is not consistent with recent observations in NaF. In particular, Fontana[18] found that the magnetic circular polarization in NaF emission was not qualitatively different from that in KF, whereas it would be if $2p'$ were lowest.

Alternatively, one can assume that in NaF there is another nonradiative decay channel during relaxation. In this case, the radiative lifetime of the relaxed state is as shown in Fig. 10.

The data interpreted this way can be fitted very well by Eq. (6) with $\alpha^2 = 0.20$ ($R = 5.6$) and $\langle \delta E \rangle = 17$ meV. This fit is shown in Fig. 10.

The field-effect data can also be interpreted consistently on this basis if one assumes that the field-induced quenching occurs during relaxation through this extra channel. Then one can assume as before that η_r for the emitting state is nearly independent of field. Using Eq. (5) to relate $\Delta M^2/M^2$ and the polarization, one gets

$$\alpha^2 = 0.03\,^{+0.2}_{-0.03} \quad . \tag{29}$$

Therefore, it seems reasonable to conclude that the emitting state in NaF is of the same character as in KF and KCl, and that the differences are due to an extra nonradiative decay channel during the relaxation process.

B. Significance of Parameters

The values of α^2 and $\langle \delta E \rangle$ determined above are listed for the three alkali halides in Table IV. These values are seen to be in reasonable agree-

TABLE IV. Model parameters.

	This work			Bogan (Ref. 4)	
	Field dependence[a]	Temperature dependence[b]			
Crystal	α^2	α^2	$\langle\delta E\rangle$ (eV)	α^2	$\langle\delta E\rangle$ (eV)
KCl	0.46	0.5	0.018	0.38	0.017
KF	0.26	0.5	0.017	0.27	0.016
NaF	0.03	0.2	0.017	~1	0.012

[a] See text for uncertainty limits.

[b] From fit to Figs. 8–10.

ment with the values obtained by Bogan from his polarization data.

Thus this very simple mixed-state model gives a surprisingly consistent and reasonable interpretation for the field and temperature dependence of F-center emission.

However, if one looks at the model to see how it might be improved, a serious inconsistency in this approach becomes apparent. That is, the mixing parameter is large and the level spacing quite small. If the mixing is due to dynamic rather than static fields, then the adiabatic or quasistatic approximation is not really valid in this limit.

Instead, one should attempt to solve for the "vibronic" states of the coupled electron-lattice system. Öpik and Pryce[19] have discussed how the $2s$ and $2p$ states might be mixed by odd-parity distortions, but they have not carried out the quite complex solution of this vibronic problem.

Nevertheless, a few comments can be made about the qualitative features of such a vibronic solution. First, there should be a series of vibronic levels in the relaxed excited state. Each vibronic level would have a different transition probability to the ground state if it contained a different admixture of $2s$ and $2p$ states. These levels would probably be separated by energies of the order of phonon energies.

Hence the significance of $\langle\delta E\rangle$ in this model is no longer as a measure of the $2s'$-$2p'$ separation, but is instead characteristic of the vibronic level spacing.

A multilevel model offers the prospect of very much better fits to the temperature-dependence data. However, to do this in other than an arbitrary fashion must await the development of solutions of this vibronic problem.

In the meantime, Bogan's mixed-state model provides a useful framework, and the only successful one at this time, for describing the properties of the relaxed excited states.

VIII. COMMENTS ON PREVIOUS LIFETIME EXPERIMENTS

There have been several experiments on F-center lifetimes prior to this, some of which were concerned with the effect of temperature and electric field. In most cases, the earlier lifetime data are in reasonable agreement with ours, although they are less precise. The drastic differences occur in the yield data, or in the interpretation placed on them. In this section we discuss these prior experiments briefly, and point out how some of these discrepancies can be understood or eliminated.

The first measurement of the temperature dependence of lifetime and yield in KCl was reported by Swank and Brown.[2] This landmark experiment gave results in remarkably good agreement with ours. Even the variation in radiative lifetime at low temperatures was noted, although with considerably less precision in their data.

A very similar temperature experiment on KF and NaF has recently been reported by Bosi *et al.*[15] For NaF, their results are in good agreement with ours. However, for KF, their lifetime and yield values are significantly different from ours. We do not understand this discrepancy.

The field effect on the lifetime in KCl was first measured by Spinolo and Fowler,[11] using dc fields up to 198 kV/cm at 4.2 °K. Their raw lifetime data are consistent with ours. However, they interpreted the change in radiative lifetime to be of opposite sign because of an incorrect assumption about the yield. Since they measured only the emission polarized perpendicular to the field, the change in intensity which they observed was in fact predominantly due to the field-induced polarization, rather than to ionization as they assumed. These authors also measured the effect of temperature on radiative lifetime at a constant field of 77 kV/cm. Again their results were affected by polarization, and the discrepancy between their data and ours seems to be due entirely to this effect.

A novel measurement of the field effect in KCl was made by Kühnert,[20] who compared the decay rate with field on and field off during the same decay cycle following pulsed laser excitation. His raw lifetime data agree with those of Spinolo and Fowler and this work, although the accuracy is probably not as good. However, Kühnert made a large correction in determining the change in radiative lifetime, to take account of the decrease in yield at high-field values. He assumed that this quenching occurred after relaxation. We would suggest that it is at least as likely that some quenching occurs during relaxation, so that $\eta_r \neq \eta_e'$.

IX. SUMMARY

The lifetime of the excited *F* center at 4.2 °K and the decrease in the radiative lifetime induced by an applied electric field and by increasing temperature have been measured in KCl, KF, and NaF with sufficient precision to test recent models for the relaxed excited states. Interpretation of the KCl and KF data was straightforward, but in NaF there appeared to be some ionization during relaxation of the excited *F* center. The results showed good agreement with the predictions of Bogan's model, in which the lowest emitting state is presumed to be 2*s*-like with a large admixture of 2*p* states. Values determined for the mixing parameter and the characteristic level separation from these data were close to the values determined in a different manner by Bogan. These values imply a strong mixing, so that further refinement of the model will require a vibronic solution of this Jahn-Teller problem.

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