TABLE III. Formation and migration energies of an interstitial He atom in LiH for two values of $\alpha(H^-)$.

$\alpha(H^-)$	Formation energy (eV) Body-centered position	Formation energy (eV) Face-centered position	Migration energy (eV)
1	2.077	2.727	0.650
11/16	3.351	3.835	0.484

defect. Because of the larger displacements, the error due to this approximation is greater when the defect is in the face-centered position than when it is in the body-centered position. Since the harmonic approximation usually underestimates the displacements, the lowering of the formation energy due to more realistic calculations should be more in the face-centered position than in the body-centered position. This would give a lower value for the migration energy as compared with the one obtained here. Thus the difference between the experimental result mentioned above and our calculated value seems to be real. This may be due to the trapping of a significant fraction of the He gas in intrinsic defects such as vacancies, divacancies, etc., which would lead to a higher value for the activation energy of diffusion. This appears to be the case for the migration of some of the rare gases in several alkali halides as shown by Norgett and Lidiard.[18] We are currently exploring this as well as the anharmonicity aspect of the present problem.

ACKNOWLEDGMENTS

We are thankful to Dr. R. Tseng and Dr. B. Holt for access to their unpublished results. We also thank Dr. J. Hardy for many stimulating discussions during the course of this work.

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[18] M. J. Norgett and A. B. Lidiard, Phil. Mag. 18, 1193 (1968).

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Stark Effects in *F*-Center Emission*†

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The effect of an applied electric field on the emission spectrum of the *F* center has been measured in the range 5–50 kV/cm and 2–150°K for six alkali halides (KCl, KF, RbCl, NaCl, NaF, and CsF). The changes induced by the field are quadratic in the field strength and isotropic with respect to the crystalline axes, and at $T \lesssim 30°K$ are as follows: an enhancement of the emission polarized parallel to the field direction with a compensating decrease of the emission polarized perpendicular to the field, a red-shift of the band in both polarizations, and a broadening in certain cases. At higher temperatures the polarization and broadening diminish. The effects in CsF are anomalously small. In several crystals, field-induced quenching of the emission due to Schottky or field ionization also appears. These results are analyzed in terms of Stark mixing in the relaxed excited state of the *F* center. The model assumes that the relaxed states consist of nearly degenerate $2p$- and $2s$-like states which are strongly mixed by crystal-field fluxtuations on the order of 200 kV/cm. For KCl, the resulting $2s'$ mixed state is lower in energy by 0.017 eV and has approximately 40% admixture of the $2p$ states. This mixed-state model is able to give a semiquantitative explanation for the Stark effects observed, as well as a consistent explanation for the magnitude and temperature dependence of *F*-center radiative lifetimes and other excited-state phenomena.

I. INTRODUCTION

UNTIL recently, the usefulness of the Stark effect in identifying optical transitions has been limited to narrow line spectra for which the electric field perturbation is larger than the linewidth. However, with the introduction of modulation and phase-sensitive detection techniques for measuring small changes in line shapes it has become possible to use the Stark effect to investigate broad-band optical transitions, such as those of the *F* center in alkali halides.

The *F* center, an electron trapped at a negative-ion vacancy, has been the object of many experimental and theoretical studies and most of its important features are by now well established.[1] It is known that optical absorption occurs from a $1s$-like $(\Gamma_1{}^+)$ ground state to a $2p$-like $(\Gamma_4{}^-)$ excited state. Recent Stark-effect experiments of Chiarotti *et al.*[2] in *F*-center absorption

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† Major portion based on a thesis submitted by one of us (L. D. B.) in partial fulfillment of the requirements for the Ph.D. degree at Cornell University, 1968.

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[1] See W. B. Fowler [in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), p. 97] for a recent review of this subject.

[2] G. Chiarotti, U. Grassano, and R. Rosei, Phys. Rev. Letters 17, 1043 (1966); G. Chiarotti, U. M. Grassano, G. Margaritondo, and R. Rosei, International Symposium on Color Centers in Alkali Halides, Rome, 1968, Abstract No. 42 (unpublished).

seem to indicate that a 2*s*-like state lies about 0.1 eV above the 2*p*-like state.

After the optical absorption takes place, the surrounding ions "relax" to a new equilibrium configuration appropriate to the excited state and the potential binding the *F*-electron changes. Consequently, the wave functions and energies of the electronic states of the excited *F* center differ from those for the ground-state lattice configuration. Much less is known about the character of these so-called "relaxed excited states."

Most treatments have assumed that the "relaxed" states are diffuse hydrogenic 2*p* states and have ignored the 2*s* state. But this is reasonable only if the relaxed 2*s* state lies well above the 2*p* states, whereas recent theoretical work[3,4] suggests that the 2*s* state may be degenerate with, or lie slightly below, the 2*p* states after lattice relaxation. In this case strong mixing is almost inevitable. Öpik and Pryce[5] pointed out that the *F* center might undergo a spontaneous Jahn-Teller distortion to remove 2*s*-2*p* degeneracy. Others[6] have considered optic phonon mixing of 2*s* and 2*p* states as a possible explanation for the anomalously long radiative lifetime of the excited *F* center.

A measurement of Stark effects in *F*-center emission should help to clarify the degree of *s*-*p* mixing in the relaxed excited states. We have carried out such an experiment using phase-sensitive detection techniques to measure changes produced in the *F*-center emission by an applied ac electric field. The effects were studied at low temperatures (2 to 150°K) and modest field strengths (5 to 50 kV/cm) to try to avoid extraneous field effects such as Schottky ionization and field ionization. Of six alkali halides investigated, KCl was studed most intensively and is analyzed as the representative case.

We show that the Stark-effect results imply that the lowest relaxed excited state is a mixture of 2*s* and 2*p* states, and that a simple model derived from these experiments can explain other features of the relaxed excited-state behavior as well.

The experimental techniques and procedures are described briefly in Sec. II, and the experimental results in Sec. III. In Sec. IV, the mixed-state model is presented and expressions are derived with which the results of this and other related experiments are analyzed.

II. EXPERIMENTAL PROCEDURES

The schematic arrangement of the Stark-effect experiment is shown in Fig. 1. A colored alkali-halide crystal is maintained at some temperature T while being subjected to an ac electric field $F(t)=F_0 \cos\omega t$. The F centers are excited with light through a partially transparent electrode, and their emission at 90° is analyzed for field-induced changes (at 2ω) as a function of wavelength for polarizations parallel and perpendicular to the field direction.

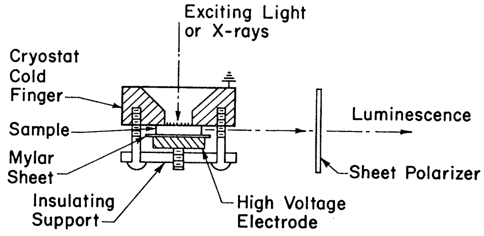

FIG. 1. Schematic cross section of the cold finger of the cryostat showing the geometry of the sample holder and the method of applying the high voltage.

Samples of KCl, NaCl, KF, and NaF from the Harshaw Chemical Co., and samples of RbCl and CsF from Semi-Elements, Inc., were used. Samples were cleaved or ground and polished to dimensions of about 10×5×1.5 mm so that the electric field could be applied perpendicular to the broad face. Most of the measurements were made for fields in the [100] direction and emission in the [001] direction. In a few cases, fields were applied in [011] or [111] directions and the emission viewed in [100] or [112] directions, respectively.

The samples were mounted as shown in Fig. 1. The ground electrode consisted of the copper body of the cold finger and a nickel screen (No. 100 mesh) which covered a $\frac{1}{4}$-in. aperture in the sample holder. The high-voltage electrode was a brass plate insulated from the sample by a sheet of 0.003-in. Mylar and held to the cold finger by nylon screws and an insulating clamp.

Most of the F centers investigated were formed by x irradiation in the cryostat at 78°K. The radiation was produced by a Norelco x-ray unit operating at 140 kV and 12 mA and was directed through one of the quartz windows of the cryostat to color the same region of the sample that would be illuminated. Exposure times were chosen to produce typical concentrations of 10^{15} to 10^{16} F centers per cm^3. The samples appeared uniformly colored through their depth and across the face of the mesh electrode. The windows showed no changes in transmission in the spectral range of interest.

Some of the KCl crystals were additively colored, then cleaved and loaded in the cryostat under safe light.

Vacuum grease was used to make thermal contact between sample and cold finger. The latter was attached to the liquid-helium bath by a variable conductivity exchange gas column. Temperatures from 15 to 200°K could be maintained with the proper combination of helium gas pressure in the exchange gas column and electrical power into a heater mounted on the sample holder. The temperature of the tail was monitored with platinum and carbon resistance thermometers. A few

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[3] W. B. Fowler, E. Calabrese, and D. Y. Smith, Solid State Commun. **5**, 569 (1967).

[4] R. F. Wood and U. Öpik, Phys. Rev. **179**, 783 (1969).

[5] U. Öpik and M. H. L. Pryce, Proc. Phys. Soc. (London) **A238**, 425 (1957).

[6] W. B. Fowler (unpublished).

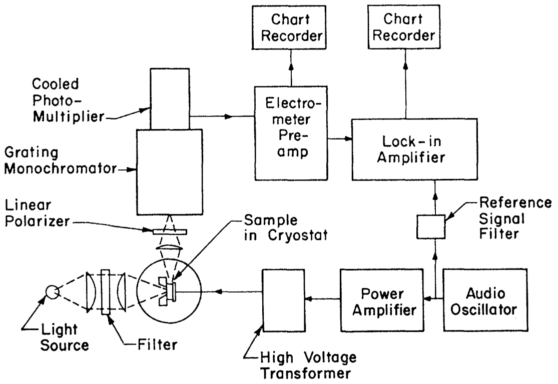

FIG. 2. Schematic diagram of the experimental setup.

measurements at 2°K were performed in a simple immersion cryostat.

The optical and electronic layout is indicated schematically in Fig. 2. Further details are given elsewhere.[7] The maximum sensitivity to field-induced changes in intensity was about two parts in 10^5 using a 1-sec integrating time constant.

In preliminary experiments in which dc rather than ac electric fields were used, and in other cases where we wished to isolate the field-induced polarization from other field-induced changes, a rotating polarizer technique was used. The analyzing polarizer was rotated and the emission analyzed for a signal at twice the frequency of rotation using the same detection equipment as before.

III. EXPERIMENTAL RESULTS

Field-induced changes in *F*-center emission were investigated for six alkali halides as a function of emission wavelength and polarization, electric field amplitude, and sample temperature. Potassium chloride was investigated most thoroughly and effects of excitation wavelength and field orientation and frequency were determined in this case. These results will be presented first as "typical."

A. KCl

1. Low-Temperature Results

A reproduction of typical raw data is shown in Fig. 3. $\Delta I_{\parallel}$ and $\Delta I_{\perp}$ are the amplitudes of the induced ac variations in photocurrent at twice the frequency of the applied electric field. These data have not been corrected for distortion due to the strongly energy-dependent instrumental response.

These uncorrected data are not suitable as they stand for a moments analysis of the field-induced changes. Nevertheless, the principal qualitative change can be seen by eye. There is an increase in parallel-polarized emission which is about twice as large as the decrease measured for perpendicular-polarized emission. Since light was collected in only one of the two perpendicular directions, the total changes in parallel and perpendicular intensity are nearly equal in magnitude and compensate each other. Thus, the dominant effect is a net polarization of the emission, rather than a net change in intensity. The effect is small, being less than 1% at this field strength.

In order to analyze the results more quantitatively we adopt the following representation for the data. The ratio $\Delta I/I$, where ΔI is the amplitude of the ac signal, is plotted as a function of photon energy as shown for a typical example in Fig. 4. This has the advantage that it eliminates the effect of instrumental response, fluctuations in excitation intensity, and so forth. The ratio $\Delta I/I$ will have the same variation with photon energy as the quantity of fundamental interest $\Delta W/W$, where W is the radiative transition probability.

Furthermore, this turns out to be a particularly simple representation when the emission band can be approximated by a Gaussian curve, as is the case for most *F* bands.

Suppose that the detected emission signal in the absence of a field can be represented as

$$I_0(x)=R(x)I_M\exp(-x^2/b^2), \qquad (1)$$

where x is the photon energy relative to the emission peak ($x=E-E_{\text{em}}$), $R(x)$ is the instrumental response function, and b is related to the full width at half-maximum of the emission intensity ($b=H/1.67$).

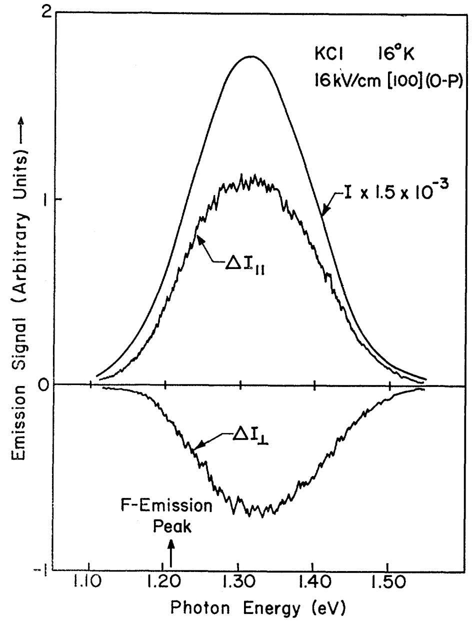

FIG. 3. Reproduction of some Stark-effect data. $\Delta I_{\parallel}$ and $\Delta I_{\perp}$ are outputs of the lock-in amplifier recorded at a gain of 670 relative to the recorded dc output of the electrometer shown as I. No corrections for instrumental response have been made.

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[7] L. D. Bogan, Ph.D. thesis, Cornell University, 1968 (unpublished).

Then if the effect of an applied field is to change the emission spectrum to

$$I(x)=R(x)I_M(1+\Delta_0)\exp[-(x-\Delta x)^2/(b+\Delta b)^2], \quad (2)$$

it is easy to show that

$$\frac{\Delta I(x)}{I_0(x)}=\Delta_0+\left(\frac{2\Delta x}{b^2}\right)x+\left(\frac{2\Delta b}{b^3}\right)(x^2-\tfrac{1}{2}b^2)+\cdots. \quad (3)$$

Here, $\Delta I(x)=I(x)-I_0(x)$, Δ_0 is the fractional change in the zeroth moment of the emission band, Δx is the change in the first moment, and $2\Delta b/b$ is the fractional change in the second moment. Thus the changes in the zeroth, first, and second moments of the band are simply related to the ordinate, slope, and curvature, respectively, of the $\Delta I/I$ curve, as shown in Fig. 4.

A plot of $\Delta I/I$ for several values of applied field is shown in Fig. 5. The fractional variation of zeroth moment as a function of applied field is shown for these data in Fig. 6(a). These are zero-to-peak field values. Since the dependence on field is seen to be quadratic, the changes induced at $2w$ are only half as large as those which would be induced by a dc field of the same amplitude. In what follows, all coefficients have been multiplied by 2 to correct for this.

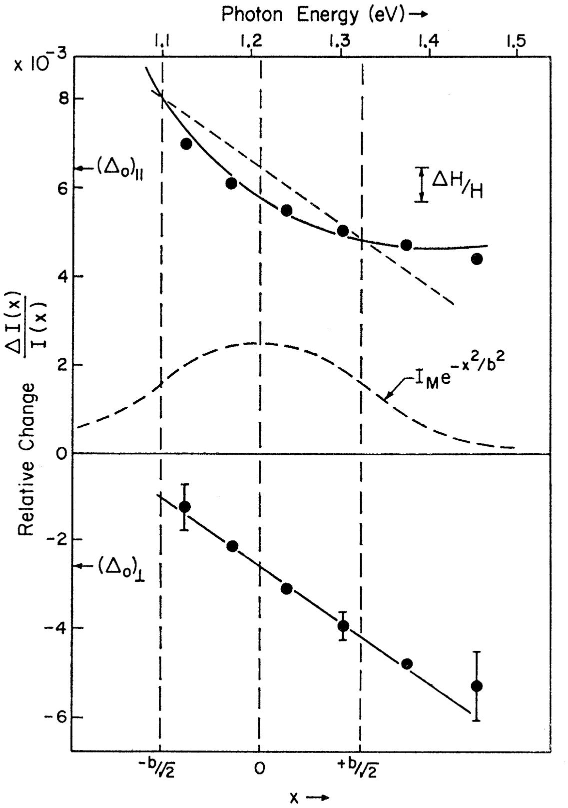

FIG. 4. Sample plot of $\Delta I/I$ data for parallel (top) and perpendicular (bottom) polarization in KCl for a [111] field of 34.3 kV/cm (zero to peak) at 16°K. Graphical analysis for determining field-induced changes in moments using Eq. (3) is shown.

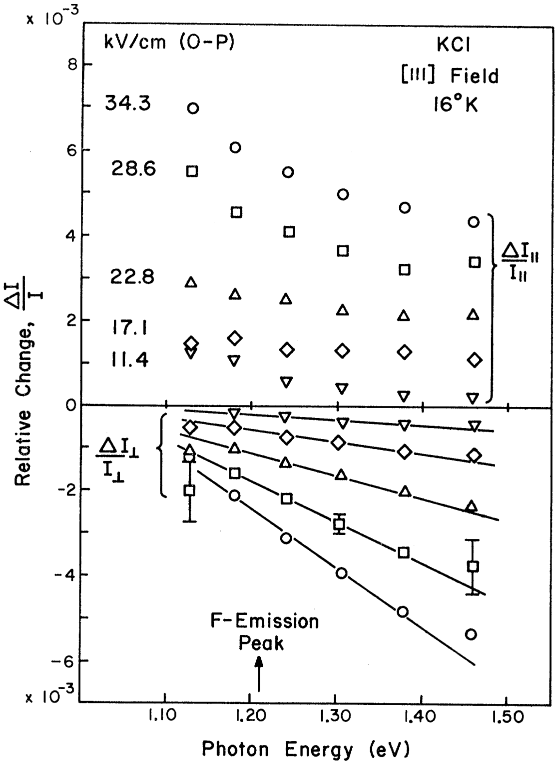

FIG. 5. Normalized Stark-effect data versus photon energy for five different [111] field strengths.

The polarization P, defined in the usual way,

$$P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp}), \quad (4)$$

can be expressed in terms of the individual ratios for field-induced changes $(\Delta I/I)_{\parallel}$ and $(\Delta I/I)_{\perp}$, since the initial intensities are nearly equal for the two. Thus

$$P\simeq\tfrac{1}{2}[(\Delta I/I)_{\parallel}-(\Delta I/I)_{\perp}]. \quad (5)$$

This gives for the polarization

$$P=(1.0\pm0.3)\times10^{-5}F^2 \quad (F \text{ in kV/cm}). \quad (6)$$

The shift of the band with field, proportional to the slope of the $\Delta I/I$ curves, is plotted in Fig. 6(b). This shift is

$$\Delta E=(-2.0\pm0.4)\times10^{-7}F^2 \text{ eV} \quad (F \text{ in kV/cm}). \quad (7)$$

The curvature of the $(\Delta I/I)_{\parallel}$ plots for KCl indicates the presence of broadening of the band. A rough estimate of the relative change in width is

$$\Delta H/H\simeq8.0\times10^{-7}F^2 \quad (F \text{ in kV/cm}). \quad (8)$$

All of these effects were seen consistently in many runs made on KCl. The results for fields in [100], [110], and [111] directions agree within experimental accuracy. The effects were shown to be independent of the wavelength, intensity, and polarization of the exciting light throughout the F-band region. No depen-

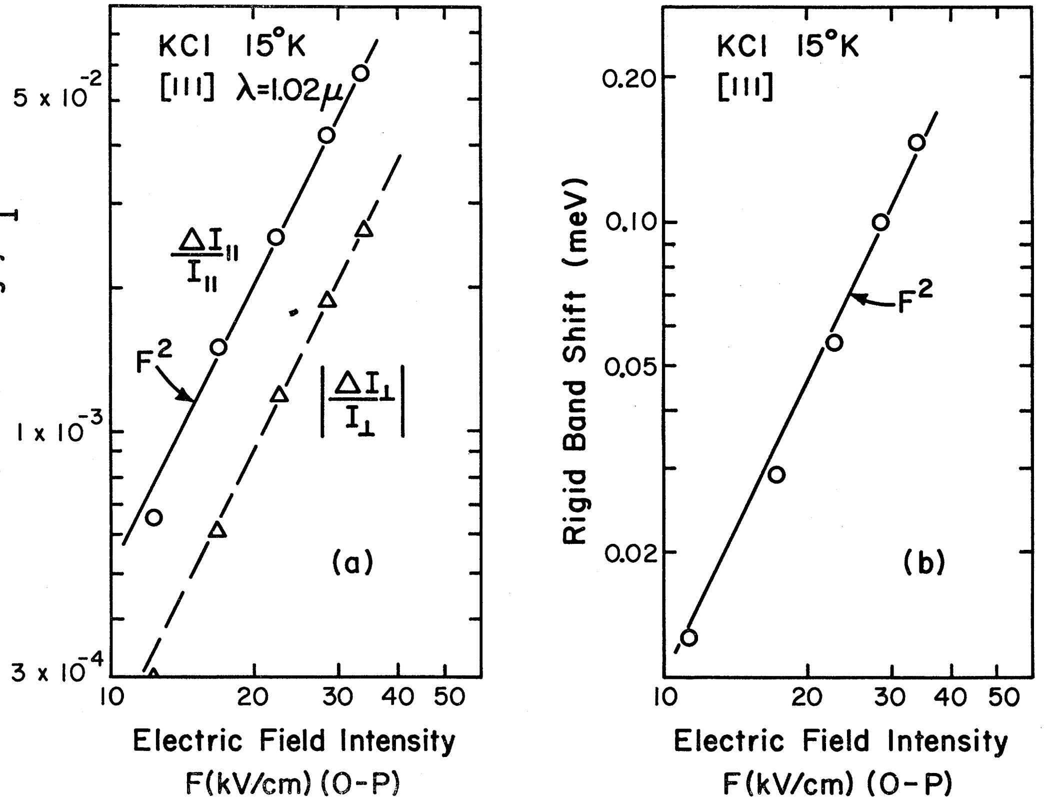

FIG. 6. (a) Dependence on field strength of the Stark effect at 0.98 μ in KCl at 15°K. (b) Dependence of ΔE on electric field.

dence on concentration was found from $1\text{–}50\times10^{15}$ cm^{-3}, but at higher concentrations M-center effects became important.

When the F luminescence was excited in the region of the K band, on the high-energy side of the F band, an additional field effect was observed, as shown in Fig. 7. This was a net decrease in intensity in addition to the same field-induced polarization. This effect is also proportional to the square of the field strength.

2. *Temperature Dependence in KCl*

The preceding section describes the field-induced effects for F-center emission for temperatures below about 30°K. Above 30°K the induced polarization decreases and the broadening disappears, but the red shift of the emission appears unchanged. These effects are illustrated in Figs. 8 and 9.

These temperature changes could be followed up to about 70°K, at which point changes due to Schottky ionization were much larger than the Stark effects, as shown in Fig. 9. The induced polarization at higher temperatures was measured using the rotating polarizer method. These data, as well as the ac field data for lower temperatures, are shown in Fig. 10.

Similar results for the field-induced changes in KCl at higher dc fields have been reported by Kühnert.[8] His results and ours are listed in Table I.

TABLE I. Stark-effect coefficients at low temperatures [10^{-6} (kV/cm)$^{-2}$].

	KCl	RbCl	KF	NaCl	NaF	CsF
Polarization $P(O)/F^2$	10±3 (13) [a]	6±2	8±3	7±2	4±1	0.2±0.1
Quenching $[(\Delta_0)_{\parallel}+2(\Delta_0)_{\perp}]/F^2$	0±2	0±2	−2±2	−19±5	−6±2	0±0.2
Red shift $\Delta E(\text{eV})/F^2$	0.2±0.05 (0.17) [a]	0.16±0.03	0.16±0.03	0.30±0.08	0.14±0.05	···
Broadening $\Delta H/HF^2$	0.6±0.3 (0.21) [a]	0.20±0.05	<0.10	···	<0.10	···

[a] Reference 8.

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[8] H. Kühnert, Phys. Status Solidi 21, K171 (1967).

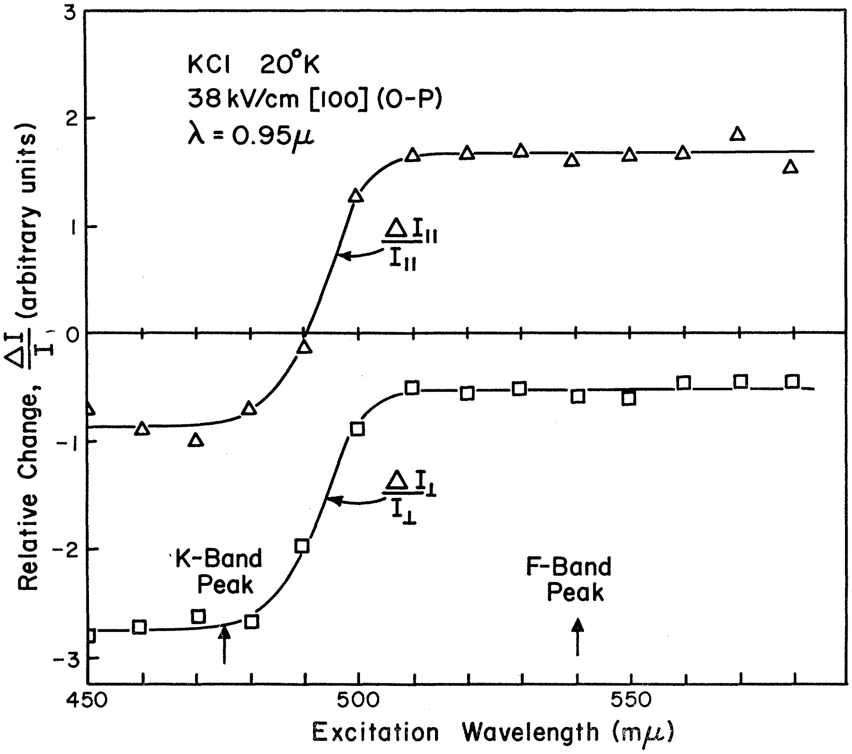

FIG. 7. Excitation spectrum for the Stark effect. Luminescence was monitored at 0.98 μ as the *F* centers were excited by light from a tungsten lamp through a monochromator.

B. Other Alkali Halides

The similarity of the Stark effects found in KF and RbCl to those in KCl is shown by the data in Figs. 11 and 12. The coefficients are listed in Table I. The temperature dependence is also similar to KCl.

In RbCl the *F*-center emission band peaks at 1.16 μ compared to 0.75 μ in KF. Since data could only be taken out to about 1.15 μ, only the high-energy half of the band in RbCl was studied. The only apparent qualitative difference among these three crystals was that no field-induced broadening was discernible in KF.

In NaF and NaCl most of the effects of field on the *F* emission were also similar to those in KCl. However, there is the important difference that the changes induced in the intensity of emission are negative for both polarizations for excitation in either the *F* or the *K* band. The magnitude of this partial quenching is proportional to the square of the field intensity. The temperature dependence of the changes induced at the peak of the band in NaF is shown in Fig. 13 and from this it can be seen that there is no strong temperature dependence of the quenching up to about 100°K. Surprisingly, no additional decrease due to Schottky ionization was detected up to 130°K.

In NaCl it was not possible to measure the temperature dependence of the Stark effects because only the extreme high-energy tail of the band could be studied, and there was a strong competing field-induced reduction in intensity.

In CsF, a band at 0.86 μ has been identified as the *F* emission band by Fulton.[9] The field-induced polarization of this band at low temperatures was smaller by

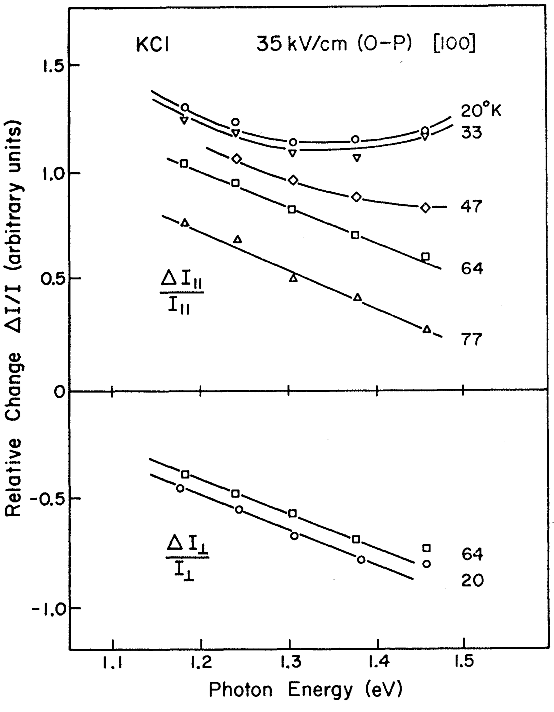

FIG. 8. Plot of the Stark-effect data for both polarizations in KCl versus photon energy for a fixed field strength but different temperatures.

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[9] T. A. Fulton, Ph.D. thesis, Cornell University, 1967 (unpublished).

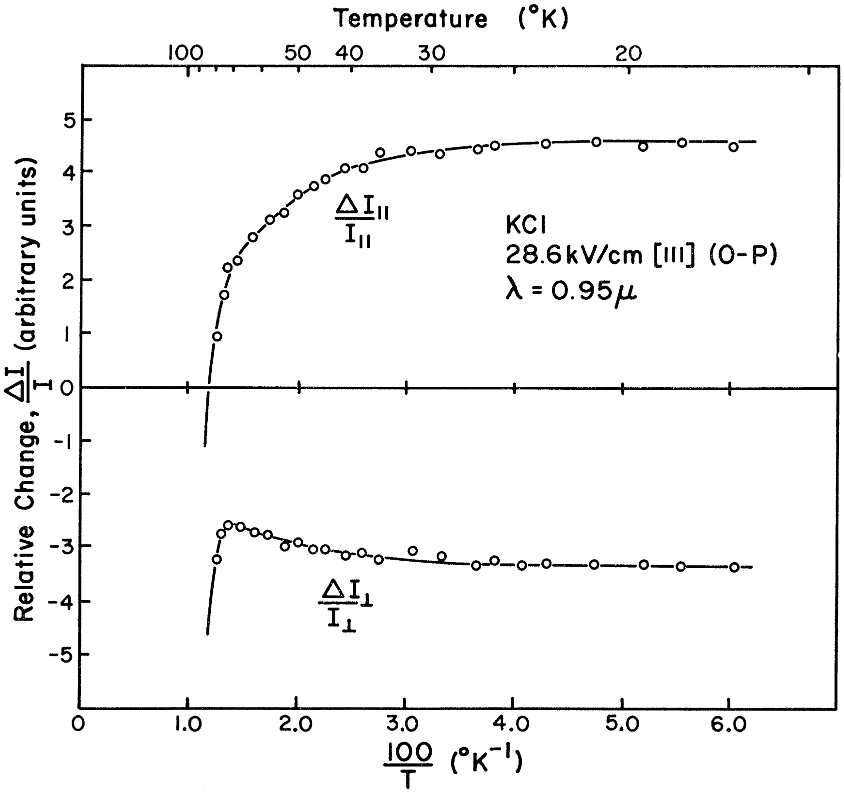

FIG. 9. Stark effect in KCl as a function of temperature. Note the onset of Schottky ionization as both polarizations go negative above 70°K.

two orders of magnitude than that in KCl, and was just barely detectable. An interesting result appeared in the measurements of field-induced quenching of the CsF emission as a function of temperature, as shown in Fig. 14.

IV. ANALYSIS AND DISCUSSION

A. Source of Effects

The experiment was designed to investigate the Stark effect in the relaxed excited state of the F center. There are, however, certain other field-induced effects which could, and in cases did, interfere. In this section, we indicate briefly why these can be eliminated as sources of the polarization.

First, we might consider whether the polarization in emission could be an effect of selective optical pumping, perhaps as a result of the Stark effect in absorption. Such effects can be dismissed since the Stark effects in absorption are much smaller than those in emission, and more significantly, because the effects observed in emission are independent of polarization in the exciting light.

Second, we might wonder whether polarization could be induced by selective ionization, either during or after relaxation. In general, the absence of field-induced quenching at low temperature makes this appear unlikely. However, even when field ionization is present, as for K-band excitation in KCl, the polarization is the same as for excitation in the F band (cf. Fig. 7); so we assume that any anisotropy induced by ionization disappears before emission occurs.

The polarization might conceivably result from some reorientation or tunneling effect in the excited state. However, if this were the case the radiative lifetime of the excited center would not change, whereas Stiles[10] recently has observed that the lifetime decreases with applied field.

The most likely source of the observed field effects appears to be a Stark mixing of the relaxed excited

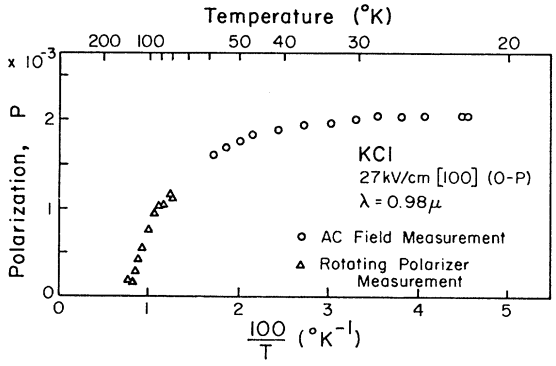

FIG. 10. Temperature dependence of the induced polarization P at higher temperatures.

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[10] L. F. Stiles, Jr., Ph.D. thesis, Cornell University, 1970 (unpublished).

states. In Sec. IV B we present a simple heuristic model which we believe suggests the explanation for the observed effects.

B. Model for Relaxed States

We propose that the relaxed excited states consist of diffuse hydrogenic states which can be described by $2s$- and $2p$-like wave functions. For simplicity, without the loss of much accuracy, higher-lying states are not included in the calculations. The $2s$ state is taken as slightly lower in energy than that of the $2p$ states, but wave functions appropriate to degenerate states are used. Fluctuating electric fields produced at the site of the F center by longitudinal optic phonons strongly mix these states such that the lifetime for radiative decay of the new $2s'$ state to the $1s$-type ground state is comparable to that of the new $2p'$ states. The observed luminescence at low temperatures is due to the radiative decay of the $2s'$ state. The interaction of the relaxed excited states with these fluctuating fields is taken as adiabatic so that at any instant of time, the states can be described as a linear combination of the $2s$ and $2p$ states.

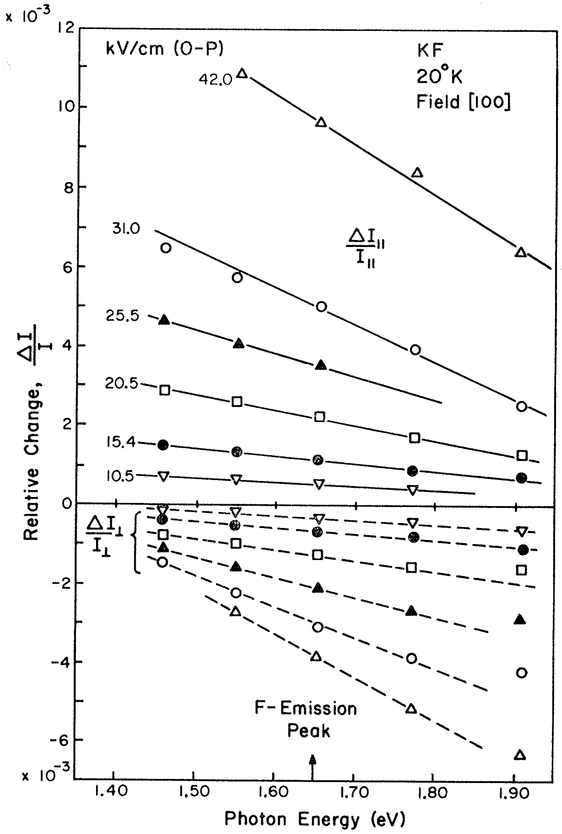

FIG. 11. Stark effects in KF at 20°K and several field strengths.

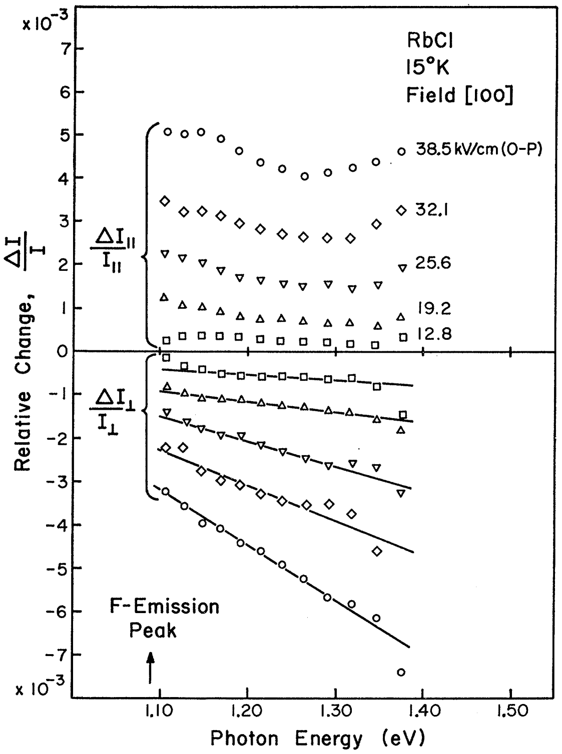

FIG. 12. Stark effects in RbCl at 15°K and several field strengths.

It is not difficult to show that the application of an external electric field will produce additional mixing of the relaxed excited states such that there will be an induced positive polarization of the luminescence, as well as a red shift and a broadening of the emission band. The electric field increases the radiative transition probability parallel to the field direction by mixing more of the appropriate $2p'$ state into the $2s'$ state. The red shift results from the repulsion of the $2s'$ and $2p'$ states when the two are mixed. The broadening is a consequence of the interaction of the electric field with the fluctuating dipole moments of the states. At low temperatures, when all the luminescence intensity is from the $2s'$ state, effects of the electric field are nearly independent of temperature, but when kT becomes comparable to the splitting of the levels, the $2p'$ state provides another channel for radiative decay and the Stark effects become temperature dependent. This qualitative description can be put on a more formal basis and gives a semiquantitative explanation of the Stark effects in F-center emission.

The only states used in this theory are $2s$, $2p_x$, $2p_y$, and $2p_z$ states which are solutions of a hydrogenic Hamiltonian H_0 for the excited F center following lattice relaxation. The fluctuating lattice fields contribute another term H' to the total Hamiltonian. This term is the interaction of the fields with the relaxed excited states of the F center and is taken as

$$H' = e\mathbf{r}\cdot\mathbf{F}_L, \tag{9}$$

where r is the electron coordinate measured from the center of the vacancy and $\mathbf{F}_L$ is a time-varying crystal

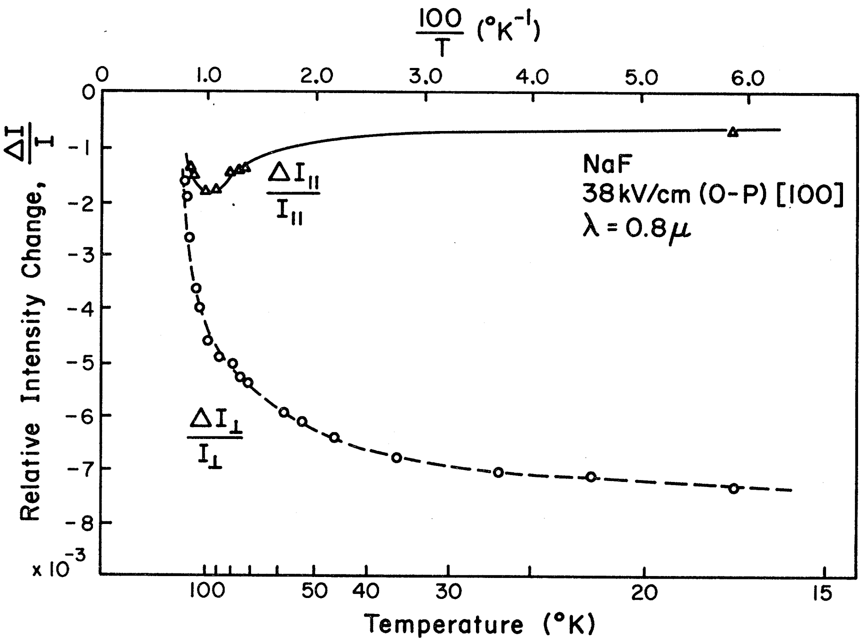

FIG. 13. Stark effect in NaF as a functon of temperature.

field (Γ_4^- component) given by

$$\mathbf{F}_L = F_L \exp(iwt)[a_1(t)\hat{\imath} + a_2(t)\hat{\jmath} + a_3(t)\hat{k}], \tag{10}$$

where $a_j(t)$ are the angle cosines of the instantaneous crystal field with the crystal axes.

The eigenstates of the total Hamiltonian H are linear combinations of the hydrogenic states and are written in the form

$$|2s'\rangle = N\{|2s\rangle + \alpha|p\rangle\}, \tag{11}$$

$$|2p_1'\rangle = N\{|p\rangle - \alpha|2s\rangle\}, \tag{12}$$

where

$$|p\rangle = a_1|2p_x\rangle + a_2|2p_y\rangle + a_3|2p_z\rangle \tag{13}$$

and

$$N = \{1+\alpha^2\}^{-1/2}. \tag{14}$$

Two other states do not contain admixtures of the $2s$ state and will be called the perpendicular states. These have the form

$$|2p_2'\rangle = b_1|2p_x\rangle + b_2|2p_y\rangle + b_3|2p_z\rangle, \tag{15}$$

$$|2p_3'\rangle = c_1|2p_x + c_2|2p_y\rangle + c_3|2p_z\rangle, \tag{16}$$

where $b_j(t)$ and $c_j(t)$ are the angle cosines defining two directions mutually perpendicular to the instantaneous crystal-field direction. These levels are shown schematically in Fig. 15. The mixing parameter α is related to the energy separation E_{sp}, of the $2p_1'$ and $2s'$ states and the fluctuating crystal-field interaction matrix element H_{sp}'. The latter is defined by

$$H_{sp}' = DeF_L, \tag{17}$$

where

$$D = \langle 2s|z|2p_z\rangle. \tag{18}$$

Substitution of these states into the total Hamiltonian yields the following relation between the three parameters:

$$H_{sp}' = -\alpha E_{sp}/(1+\alpha^2). \tag{19}$$

The lifetime of the $2s'$ state may be written as[1]

$$\frac{1}{\tau_s} = n\frac{4E_{\text{em}}^3 e^2}{3\hbar^4 c^3} M_s^2, \tag{20}$$

where n is the index of refraction of the host crystal and E_{em} is the energy of the peak of the emission band. The squared dipole matrix element M_s^2 is defined by the relation

$$M_s^2 = \sum_{j=1}^{3} |\langle 1s|x_j|2s'\rangle|^2 = \sum_{j=1}^{3} \frac{\alpha^2}{3(1+\alpha^2)} |\langle 1s|x_j|2p_j\rangle|^2$$
$$= [\alpha^2/(1+\alpha^2)]M^2, \tag{21}$$

where

$$M^2 = |\langle 1s|x|2p_x\rangle|^2. \tag{22}$$

For convenience, the external electric field is assumed to be applied in the z direction and the amount of $2p_z$ state mixed into the $2s'$ state from the $2p'$ states is denoted by the parameter $\Delta\alpha$. The applied field intensity F_A is assumed to be small compared to the magnitude of the crystal-field fluctuations so that perturbation techniques may be used in the calculations of the Stark effect. The expression for $\Delta\alpha$ from perturbation theory is

$$\Delta\alpha = eDF_A/(1+\alpha^2)^{1/2}E_{sp}. \tag{23}$$

Now the expressions for the relaxed excited state must be rewritten

$$|2s'\rangle = N'\{|2s\rangle + \alpha|p\rangle + \Delta\alpha|2p_z\rangle\}, \tag{24}$$

where

$$N' = (1+\alpha^2+\Delta\alpha^2)^{-1/2}. \tag{25}$$

Thus the Stark effect should cause a change in the lifetime given by

$$\Delta\tau_s/\tau_s = \Delta\alpha^2/\alpha^2(1+\alpha^2). \tag{26}$$

The decrease in the lifetime of the $2s'$ state is a result of the increase in the transition probability for radiative decay by the emission of light polarized parallel to the z direction. No changes take place in the x and y directions. As a consequence, the polarization of the luminescence will be given by

$$P = \tfrac{3}{2}\left(\frac{\Delta\alpha^2}{\alpha^2}\right) = \frac{\tfrac{3}{2}(F_A/F_L)^2}{(1+\alpha^2)^3}. \tag{27}$$

A measurement of luminescence decay time following pulsed excitation should detect the same field-induced decrease in lifetime for both polarizations, while a measurement of field-induced changes under steady-state excitation should detect a polarization, but no net change in intensity. From Eqs. (26) and (27) it is easily seen that the polarization is related to the change in the lifetime by

$$P = -\tfrac{3}{2}(1+\alpha^2)\Delta\tau_s/\tau_s. \tag{28}$$

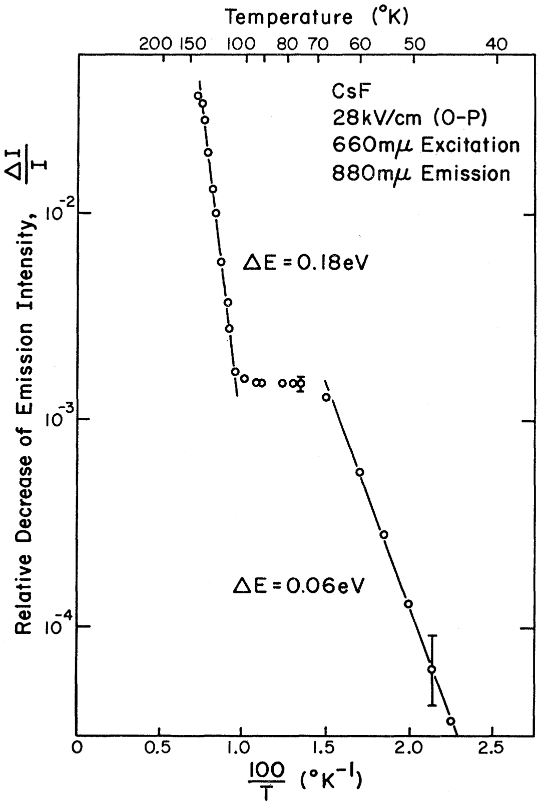

FIG. 14. Temperature dependence of the field-induced quenching of F emission in CsF.

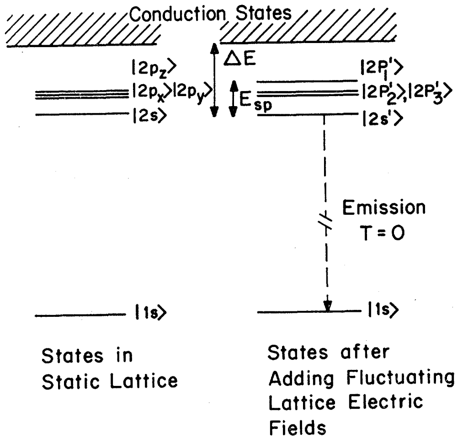

FIG. 15. Schematic energy-level diagram for the mixed state model of the excited F center.

The polarization should be independent of the direction of the applied field with respect to the crystal axes because the diffuse hydrogenic states sample the bulk of the crystal and as a result the properties of the relaxed state are not significantly influenced by the cubic environment of the vacancy itself. Also the assumed randomness of the fluctuating crystal fields will help to maintain the isotropy of the Stark effects.

Since the $2s'$ state is partially p-like, it will have a fluctuating dipole moment. The external field will interact with this moment to shift the energy of the state. This shift is given by

$$\Delta E_s^{(1)} = \langle 2s' | ezF_A | 2s' \rangle = 2e\alpha a_3(t) DF_A/(1+\alpha^2). \tag{29}$$

The largest shifts should occur for those $2s'$ states which have most $2p_z$ component $[a_3(t) \simeq 1]$ and which emit light polarized in the z direction.

Since the time and spatial average of the angle cosine $[a_3(t)]$ is zero, the average shift of the emission band is zero. However, some F centers have equal and opposite shifts due to variation of the instantaneous lattice field throughout the crystal, and these shifts do appear as a broadening of the emission band for light polarized parallel to the applied field. Because the shift is much smaller than the width of the band, the width will increase quadratically with the applied field intensity. Assuming a gaussian band, the relative change in half-width is

$$(\Delta H/H)_{\parallel} = 3.71 e^2\alpha^2 D^2 F_A{}^2/H^2(1+\alpha^2)^2. \tag{30}$$

Another Stark shift results from the $2s'$-$2p'$ repulsion due to additional mixing of the excited states by the applied field. This shift, which does not average to zero, is

$$\Delta E_s^{(2)} = D^2 F_A{}^2 e^2 (1+\tfrac{2}{3}\alpha^2)/(1+\alpha^2)^2 E_{sp}. \tag{31}$$

It should appear for both polarizations.

Temperature dependence will enter this model in two significant ways. First, the mixing of s- and p-like states will increase from the value appropriate for the zero-point amplitude of the odd-parity modes as these modes become thermally excited. Second, an increase in temperature may cause the higher p-like states to become thermally populated, leading to emission at nearly the same energy but with very different characteristics. In what follows we shall assume that the second effect is dominant, since the energy separations turn out to be quite small.

The two important factors that determine the exact form are the mean energy of separation $\bar{E}$ of the $2s'$ and $2p'$ states and their relative probabilities for radiative decay. It can be shown that the mean energy is given by

$$\bar{E}=E_{sp}(1+\tfrac{1}{3}\alpha^2)/(1+\alpha^2). \tag{32}$$

Rate equations were solved for the radiative lifetime assuming that the three $2p'$ states are degenerate and lie an energy $\bar{E}$ above the $2s'$ state, and assuming that the relaxation rate between the states is fast compared to the inverse lifetime for emission.[11]

The result for the radiative lifetime of the excited F center is

$$\tau_R=\tau_s\left(\frac{1+3e^{-\bar{E}/kT}}{1+3(\tau_s/\tau_p)e^{-\bar{E}/kT}}\right), \tag{33}$$

where

$$\tau_s/\tau_p=(1+\tfrac{2}{3}\alpha^2)/\alpha^2. \tag{34}$$

The mixing parameter α will usually depend upon temperature unless the mixing is nearly complete ($\alpha\sim1$). For the F center, we will find that we are close to this limit, so we ignore this temperature dependence. (The opposite extreme has been considered by Tomura *et al.*[12] who consider this temperature dependence to be the dominant effect.)

The temperature dependence of the Stark effects will arise primarily from thermal depopulation of the $2s'$ state. For instance, the temperature dependence of the polarization is predicted to be

$$P(T)=\frac{(1-e^{-\bar{E}/kT})P(O)}{1+3(\tau_s/\tau_p)e^{-\bar{E}/kT}}, \tag{35}$$

on the assumption that there is a compensating field-induced polarization for the $2p'$ states and that the effect of thermal ionization can be ignored.

The red shift and broadening with applied field should also decrease with increasing temperature.

C. Comparison with Experiment

If we were to take the model literally, we could estimate *a priori* some of the model parameters by a suitable scaling of hydrogenic energies and matrix elements. Instead, we shall deduce the parameters empirically from the experimental results for the field-induced polarization $P(T)$. We use KCl as the test case.

1. *Stark Effects in KCl*

The temperature dependence of the field-induced polarization can best be exhibited by rewriting Eq. (35) as

$$P(O)/P(T)-1\simeq Ae^{-\theta/T}, \tag{36}$$

where $A=3\tau_s/\tau_p$ and $\theta=\bar{E}/k$, and where we have assumed that $A\gg1$.

Figure 16 shows that the measured polarization does appear to have this dependence, with the parameters

$$A=10\pm4 \tag{37}$$

and

$$\theta=(207\pm20)^\circ\mathrm{K}. \tag{38}$$

From Eqs. (32) and (34) these yield two fundamental parameters for the model:

$$\alpha=0.6\pm0.2 \tag{39}$$

and

$$E_{sp}=0.021\pm0.005\ \mathrm{eV}. \tag{40}$$

The value of α implies that the $2s'$ state has about 40% admixture of $2p$ states. The value of E_{sp} implies that the $2s'$ state lies about 0.021 eV below the $2p_1'$ state.

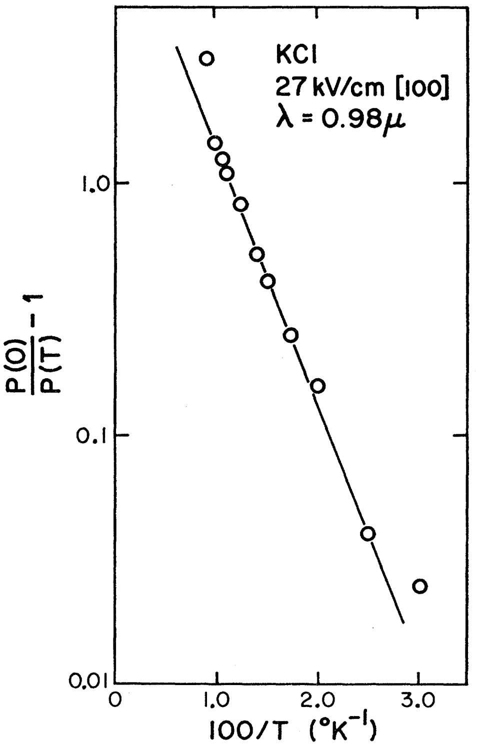

FIG. 16. Temperature dependence of the field-induced polarization for F emission in KCl.

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[11] M. Bertolaccini, L. Bosi, S. Cova, C. Busolati, and G. Spinolo, International Symposium on Color Centers in Alkali Halides, Rome, 1968, Abstract No. 20 (unpublished).

[12] M. Tomura, T. Kiada, and S. Honda, J. Phys. Soc. Japan **23**, 454 (1967).

TABLE II. Shift and broadening coefficients for KCl.

	$\Delta E/F^2$ [10^{-8} eV (kV/cm)$^{-2}$]	$\Delta H/HF^2$ [10^{-8} (kV/cm)$^{-2}$]
This experiment	20 ± 5	60 ± 30
Kühnert[a]	17	21
Model	5 ± 3	1.9 ± 1.5

[a] Reference 8.

The third fundamental parameter, the extra mixing produced by unit applied field, can be determined from the experimental value for the polarization at low temperature, using Eq. (27). To make the connection with the model it is really the local field that is needed, but we make the assumption that this is the same as the bulk field for the rather diffuse states of the excited F center. Then

$$\Delta\alpha = (1.6\pm0.6)\times10^{-3}\times F_A \quad (F_A \text{ in kV/cm}). \qquad (41)$$

Using these three parameters secondary features such as the red shift and broadening can be predicted. The predicted coefficients are compared with the measured values in Table II. The agreement is at best qualitative. The temperature dependence of these coefficients differs from that of the polarization, and also from that of the model.

Significance of parameters. We now examine whether the parameters chosen to explain the primary effects are reasonable. An equivalent set of parameters can be derived from Eqs. (23) and (27). These are the $2s$-$2p$ dipole matrix element D, the lattice field intensity F_L, and the energy spacing E_{sp}. These are

$$D = 4\pm2\ \text{Å}, \qquad (42)$$

$$F_L = 240\pm100\ \text{kV/cm}, \qquad (43)$$

and

$$E_{sp} = 0.021\pm0.005\ \text{eV}. \qquad (44)$$

If we consider the excited F center as a hydrogenic system imbedded in a dielectric continuum, then the matrix element D is given by

$$D = \langle 2s|z|2p_z\rangle = 3Ka_0, \qquad (45)$$

where a_0 is the Bohr radius and K is an effective dielectric constant. Taking the high-frequency dielectric constant for KCl ($K=2.19$) would yield $D=3.36$ Å, in surprisingly good agreement with experiment. On the other hand, we would expect the effective dielectric constant for the relaxed state to be larger, and recent estimates[3,4] would place D at two to four times this value.

To check the parameter F_L, a calculation was made[7] to determine from first principles the effective lattice field due to longitudinal optic phonons. Similar calculations by Redfield[13] and by Conway *et al.*[14] gave fields of order 1000 kV/cm at a lattice site, but these are not appropriate for the fields at defects with rather extended wave functions. Instead, for the relaxed excited state of the F center, the field was estimated by summing the effects of all LO modes with wavelengths longer than twice the mean diameter of the state. Modes of shorter wavelength produce nonuniform fields over the extent of the states and their effects are assumed to cancel to zero. Using this criterion we take

$$\lambda_{\min} \simeq 4\langle r_{2s}\rangle = 4\times(6Ka_0) \simeq 26\ \text{Å} \simeq 4a, \qquad (46)$$

where a is the lattice constant. For this cutoff the estimated effective field is $\sim$400 kV/cm. The empirical value for F_L is obtained if the cutoff is made at $\lambda_{\min}\sim5a$, so this field seems a reasonable value.

The value for E_{sp} is probably the most significant result of the analysis. Originally it was thought that the $2s$ state lay well above the $2p$ state both in absorption and emission. However, Chiarotti *et al.*[2] have reported recently that their Stark-effect emasurements in F absorption indicate that the $2s$ state there is only about 0.1 eV above the $2p$ state. Calculations by Fowler *et al.*[3] and by Wood and Öpik[4] for the energies of the states after relaxation now indicate that the relaxed $2s$ state may be degenerate with, or even slightly lower than, the relaxed $2p$ state. The present experiment seems to indicate that not only is the $2s$-like state lower, but the separation is so small that the states are very strongly mixed by phonons.

2. *Comparison with Other Excited-State Experiments*

There have been a number of experiments recently to try to determine the properties of the relaxed excited states of the F center. Most of these have been interpreted on the basis of a diffuse $2p$-like state being the emitting state. In this section, we indicate briefly how these results can be explained as well with the mixed-state model.

(*a*) *Lifetime of excited state.* The mixed-state model attributes the long radiative lifetime of the excited F center in part to the reduced transition probability from the $2s'$ state. Its low-temperature behavior, as given by Eqs. (20), (33), and (34), should be determined by the same parameters deduced from the Stark-effect results.

In particular, the limiting lifetime at low temperature should be

$$\frac{1}{\tau_s} = \frac{n4E_{\text{em}}{}^3e^2}{3\hbar^4c^3}\,\frac{\alpha^2}{1+\alpha^2}M^2, \qquad (47)$$

where n is the index of refraction at the emission energy E_{em} and M is the $2p$-$1s$ dipole matrix element. Inserting values for KCl, and using the most recent experimental

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[13] J. Conway, D. Greenwood, J. Krumhansl, and W. Martienssen, J. Phys. Chem. Solids **24**, 239 (1963).

[14] D. Redfield, Bull. Am. Phys. Soc. **9**, 228 (1964).

value for the lifetime[15]

$$\tau(0°\mathrm{K})\simeq 0.715\times 10^{-6}\ \mathrm{sec}, \tag{48}$$

we find an empirical value

$$M^2=(25\pm 8)\times 10^{-18}\ \mathrm{cm}^2. \tag{49}$$

This is reasonably consistent with a recent theoretical estimate by Wood and Öpik[4] which predicts a value for M^2 of 50 or 300×10^{-18} cm^2 depending on the degree of ionic relaxation.

The temperature dependence of the lifetime should involve the same parameters as the Stark polarization, at least in the range before thermal ionization becomes important. Equation (33) predicts that the lifetime should decrease in the range 40–100°K *before* the onset of thermal ionization, whereas the usual p-state model[16] assumes that it will be constant in this range. The recent experiment of Stiles *et al.*[15] confirmed this prediction and found a variation of τ_R which is consistent with the mixed-state model. A detailed analysis of the lifetime results will be presented by Stiles in a forthcoming paper.

(*b*) *Field ionization.* Spinolo and Fowler[17] have measured the electric field dependence of the lifetime and the quantum efficiency for luminescence of the relaxed excited states of the F center in KCl. They interpreted their data in terms of an electric-field-induced tunneling out of the diffuse relaxed p state into the conduction band. However, their geometry was such that only emission polarized perpendicular to the field was observed, so that changes in luminescence yield could have been due to either a decrease in η or to polarization. Extrapolation of the predicted change in lifetime due to the Stark effect into the field range of their data shows that below 150 kV/cm their results are probably due to the Stark effect and very little to field ionization. Figure 17 shows some of the data for change in lifetime and intensity reported by Spinolo and Fowler, along with the predictions of Eq. (28). Above 150 kV/cm their data show an increase larger than quadratic in the field, and this is probably caused by the onset of field ionization. Their analysis should be applied to this extra part.

(*c*) *Stress-induced polarization.* Hetrick and Compton[18] measured the effect of uniaxial stress on the polarization of F emission. They found an effect which was independent of temperature but dependent on crystal orientation, and this they interpreted as mixing of d state into the ground-state wave function. The only assumption they require for the excited state is that it have (some) p-like character and that it be rather diffuse (thus insensitive to the applied stress). The mixed-state model satisfies both conditions and the rest of their interpretation carries over to this model intact.

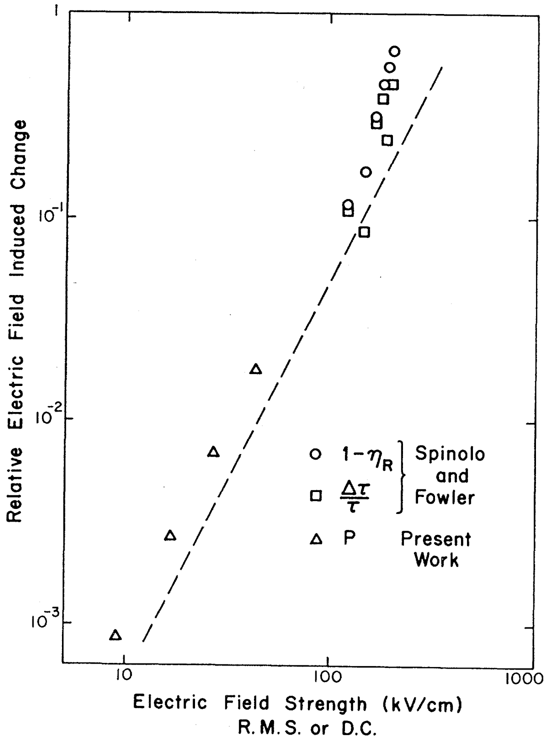

FIG. 17. Comparison of the prediction (dashed line) for field-induced changes in F-center lifetime with the data of Spinolo and Fowler (Ref. 17) for KCl at 4.2°K.

(*d*) *Lifetime of F_A center.* Spinolo and Brown[19] measured the lifetime of the F_A center in KCl, i.e., an F center perturbed by a foreign Na$^+$ ion at one of the nearest-neighbor sites. They argued that since this strong perturbation produced only a 10% decrease in lifetime, a "metastable" state was unlikely. However, now that we know both the effect of stress and electric field on F emission, the 10% effect for this perturbation is quite reasonable, and is consistent with the mixed-state model.

(*e*) *Absorption in excited state.* Park and Faust[20] have measured the spectrum of absorption from the excited states of the F center in KI and found that most of the oscillator strength is in transitions to states below the conduction band. Fowler *et al.*[3] have calculated the oscillator strength for the $2p$ to $3d$ transition assuming that the relaxed excited state is a diffuse p-like state and found it to be in order-of-magnitude agreement with the results of Park and Faust. The oscillator strength of a $2s$ to $3p$ transition in the hydrogenic approximation is only 37% smaller than that of the $2p$ to $3d$ transition. Consequently, the mixed-state model agrees as well with the measured excited-state absorp-

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[15] L. F. Stiles, Jr., M. P. Fontana, and D. B. Fitchen, Solid State Commun. **7**, 681 (1969).

[16] R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).

[17] G. Spinolo and W. B. Fowler, Phys. Rev. **138**, A661 (1965).

[18] R. Hetrick and W. D. Compton, Phys. Rev. **155**, 649 (1967).

[19] G. Spinolo and F. C. Brown, Phys. Rev. **135**, A450 (1964).

[20] K. Park and W. Faust, Phys. Rev. Letters **17**, 137 (1966).

TABLE III. Temperature-dependence parameters.

Crystal	θ(°K)	A
KCl	210±20	10±4
RbCl	180±20	6±3
KF	190±20	13±4
NaCl	···	···
NaF	140±20	3±3
CsF	···	···

tion. The agreement may be even better when the transitions to states higher than the $3p$ are considered also.

(*f*) *Blue shift of emission band.* If the relaxed excited state is predominantly $2s$-like and the $2p$ states are nearby as suggested then one would expect a blue shift of the emission band as more of the luminescence originates from the $2p$ states at higher temperatures. No such shift is observed but, in this case, the shift would be too small to detect. Estimates indicate that at 100°K the shift would be only 0.012 eV, while the red shift due to thermal expansion is considerably larger.

3. *Stark-Effect Results in Other Alkali Halides*

The field-induced polarization and shift of the *F*-emission band were similar in magnitude and temperature dependence for all the alkali halides studied in this experiment except CsF which showed almost no effect. The data for these alkali halides are not as complete as for KCl, and they have not been tested quantitatively for self-consistency. In particular the key parameters α and E_{sp}, which must be determined from the temperature-dependence parameters of the polarization listed in Table III, have very large uncertainties in these cases. Nevertheless, some qualitative comments can be made.

First, in the three other cases where θ and A were determined, these yield values for α and E_{sp} which are quite similar to those for KCl. In each case the mixing coefficient is large ($\alpha\sim 1$) and $k\theta$ is comparable to phonon energies. These common features suggest that a more accurate model for the relaxed excited-state behavior should treat this system in terms of vibronic states. This approach will be considered in a later publication.

The exceptionally small Stark effect observed for CsF is probably related to other unusual properties of its excited state found by Fulton.[9] This result and the unusually short radiative lifetime of 50 nsec [21] both seem to imply that the relaxed excited state in CsF is not a $2s$-like state. We might speculate that the large spin-orbit splitting which Fulton found to persist in the relaxed states is sufficient to prevent the $2s'$ state lying lowest.

The two separate activation energies for the Schottky ionization in CsF (cf Fig. 14) are in reasonable agreement with the two activation energies determined by Fulton from photoconductivity data, and support his interpretation of two different relaxed excited states.

Finally, the extra field-induced quenching of the luminescence observed in NaF and NaCl probably has the same origin as the quenching observed for *K*-band excitation in KCl. That is, field ionization during the process of lattice relaxation probably causes this decrease. Both crystals are known to have very small activation energies for thermal quenching of *F* luminescence, suggesting that field-induced quenching should be easy.

V. SUMMARY

The effect of an applied electric field on the emission spectrum of the *F* center has been determined for six alkali halides. The results have been analyzed in terms of a Stark effect in the relaxed excited state of the *F* center. The model presented assumes a $2s$-like state about 0.02 eV below the $2p$-like states, and strongly mixed with them by crystal-field fluctuations on the order of 200 kV/cm in amplitude. This model is able to give a semiquantitative explanation for the Stark effect observed, as well as a consistent explanation for the magnitude and temperature dependence of the radiative lifetime and other excited-state phenomena.

ACKNOWLEDGMENTS

We wish to thank Dr. L. F. Stiles, Jr., Dr. M. P. Fontana, Dr. T. A. Fulton, and Professor W. B. Fowler for valuable discussions.

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[21] T. A. Fulton and D. B. Fitchen, Phys. Rev. B 1, 4011 (1970).