[except that (18c) is badly violated in some cases involving row-I atoms], but the parameters would be chosen to fit α and β for a more appropriate crystal. For example, the elastic constants of BN would be predicted from those of diamond.

In summary, the elastic properties of the sphalerite structure semiconductors, especially the shear moduli, have been shown to follow simple trends as functions of the ionicity f_i, as defined by Phillips and Van Vechten. These results (Figs. 2–4) give quantitative form to the observations made by Keyes.[5] Also the present work has presented a simple theory of the elastic constants of tetrahedrally coordinated crystals which involves only two parameters fitted to the elastic data. The theoretical formulation yielded four important results; (a) a relation [Eq. (13)] among the elastic constants and the optical effective charge which was shown to be satisfied to $\sim 10\%$, (b) a calculation of the internal strain parameter[9,11] ζ from the elastic data, (c) the trends (as function of f_i) in the fitted parameters α, β, and S which

supports the interpretation given them in the theory. and (d) a set of formulas from which the elastic constants of a ZB crystal can be predicted from its bond length and ionicity[7] with an expected accuracy of 10%.

Note added in proof. The suggestion made in the present paper that the experimental elastic constants of ZnSe were erroneous has been verified. Recent measurements reported by Lee[17] yield $C_{11}=8.59$, $C_{44}=4.06$, and $C_{12}=5.06$. With the new constants Eq. (13) is satisfied to 11% in accord with similar compounds. No other results for ZnSe are greatly changed. The author is indebted to Dr. Y. S. Park for bringing to his attention the work of Dr. Lee.

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It is a pleasure to acknowledge many helpful conversations with J. C. Phillips and J. A. Van Vechten.

[17] B. H. Lee (to be published).

F Center in Cesium Fluoride : Properties of the Optically Excited Center*

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Studies of the luminescence, photoconductivity, Schottky ionization, bleaching, and ground-state repopulation of the optically excited F center in CsF are reported, with these main results: (a) Excitation in the F absorption band centered at 1.88 eV gives rise with high efficiency to a luminescence band (at 1.43 eV) whose unusual properties include the small Stokes shift (0.45 eV), narrow low-temperature width (0.10 eV), and short lifetime (50 nsec). (b) Photoconductivity, Schottky ionization, and optical bleaching show a wavelength dependence in the F-band region. Thermal ionization of the optically excited center is found to be more efficient for excitation in the high-energy component of the triplet F absorption band, which corresponds to the $P_{1/2}$ level of the spin-orbit-split P-like excited states. This implies that the lattice relaxation processes are influenced by the initial state. (c) The characteristic time for return to the ground state for an optically excited F center is found to be 1.0 μsec, much longer than the luminescence lifetime. This suggests the occurrence of a bottleneck in the lattice relaxation following the emission.

I. INTRODUCTION

THE unusual properties of the optical absorption of the F center in cesium fluoride have been described in a previous paper,[1] in which a number of

phenomena not usually associated with F-center optical properties were shown to be important. Among these are a combination of spin-orbit and Jahn-Teller interactions of comparable strength in the P-like excited states, leading to an optical-absorption band (F band) consisting of three narrow resolved components, on which structure due to discrete optical-phonon transi-

[1] T. A. Fulton and D. B. Fitchen Phys. Rev. **179**, 846 (1969).

tions can be seen. In the present paper we examine the results and interpretation of several experiments which concern the behavior of this center after its excitation by optical absorption. The experiments are of five types: luminescence, photoconductivity, Schottky ionization, optical bleaching, and ground-state repopulation (GSR). As in the case of optical absorption, several novel results are encountered, not all of which are understood.

The connection between the properties of the center after optical excitation and those of the unexcited center is not direct, because of the intervening lattice relaxation. The potential binding the electron to the halide vacancy, being due solely to the surrounding lattice ions, is sensitive to their equilibrium positions and particularly those of the nearer neighbors. These positions are in turn influenced by the charge distribution and hence the state of the F-center electron. When the electron makes an optical transition from the ground to the excited state, the neighboring ions, whose positions are semiclassically regarded as fixed in the transition, subsequently adopt new equilibrium positions consistent with the excited-state charge distribution, i.e., the lattice relaxes. The binding potential is correspondingly modified and so are the electronic energy levels and wave functions. The electronic states and energy levels and the lattice configuration are referred to as "relaxed" or "unrelaxed" depending on whether the ion configuration corresponds to the electronic excited or ground states. The relaxed configuration is thought to be established in a time $<10^{-10}$ sec following absorption, so that experiments on the luminescence, photoconductivity, etc., generally give results characteristic of the relaxed states rather than the unrelaxed. In F centers the lattice relaxation is typically so large that the properties of the relaxed and unrelaxed states are quite different. To a considerable extent this turns out to be true for the F center in cesium fluoride as well.

The results to be described contain two particularly unusual features. First, the lattice relaxation is found to be affected by the spin-orbit splitting of the excited P-like states described in Ref. 1, and proceeds differently for excitation to the $P_{1/2}$ and $P_{3/2}$ states. Second, there exists an unexplained bottleneck in the decay of the optically excited center to the unrelaxed ground state, apparently in the transition from the relaxed to the unrelaxed ground state *following* luminescence. There are also several extreme properties of the luminescence, such as a small Stokes shift, narrow bandwidth and short lifetime, whose interpretation must await a resolution of the bottleneck problem.

In Sec. II we discuss the models of F-center behavior used to understand the five types of experiments, with modifications appropriate to CsF. The experiments and their results are presented in Sec. III. The implications of these results in terms of the models of Sec. II are

presented in Sec. IV. In Sec. V we discuss the possible physical nature of the states responsible for this behavior in CsF. Section VI presents some suggestions for future work in this system.

II. THEORY

A. One-Level Model

A commonly used schematic model of the F-center behavior after optical excitation is shown in Fig. 1(a). The electron, initially in its unrelaxed ground state, undergoes a transition to the unrelaxed excited state, absorbing a photon. The lattice relaxes in a nominal time $<10^{-10}$ sec and the center reaches its relaxed excited state.

From this point the electron may be thermally ionized, leading to photoconductivity, or it may return to the ground state. In most F centers this return is predominantly a radiative transition to the relaxed ground state followed by lattice relaxation which restores the unrelaxed ground state. The radiative transitions result in a strong luminescence band which is Stokes shifted by the energy consumed in the lattice relaxations and broadened by electron-lattice interactions just as is the F-absorption band. Typical values are Stokes shifts of 50% of the absorption energy and low-temperature widths of 0.2–0.3 eV.
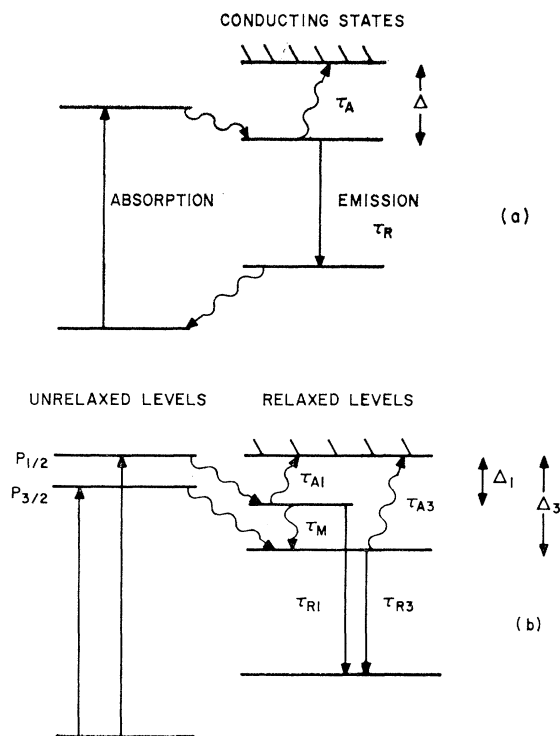

FIG. 1. Decay schemes in the (a) one-level and (b) two-level models. Vertical straight lines indicate radiative transitions and wavy lines nonradiative transitions. Characteristic times and activation energies for each process are shown.

A standard approach[2] is to assume that the radiative and nonradiative decays to the ground state proceed with temperature-independent characteristic times τ_R and τ_N, i.e., (transition probabilities)/(unit time) $1/\tau_R$ and $1/\tau_N$. The thermal ionization process is taken as a simple thermally activated process with characteristic time $\tau_I = \tau_A e^{\Delta/kT}$, where $1/\tau_A$ is a temperature-independent attempt frequency, Δ the activation energy, and kT Boltzmann's constant times the temperature. The absolute quantum efficiency for luminescence $\bar{\eta}_R$, defined as (number of centers decaying by radiative transitions/unit time)/(number of centers excited/unit time) is then

$$\bar{\eta}_R(T) = (1/\tau_R)(1/\tau_R + 1/\tau_N + 1/\tau_I)^{-1}. \quad (1)$$

We are neglecting here and hereafter, perhaps not justifiably, any F luminescence due to recombination of ionized electrons with vacancies. The experimentally measured quantity is actually the efficiency relative to the low-temperature efficiency, $\eta_R(T) = \bar{\eta}_R(T)/\bar{\eta}_R(0)$, or

$$\eta_R(T) = (1/\tau_R + 1/\tau_N)(1/\tau_R + 1/\tau_N + 1/\tau_I)^{-1}. \quad (2)$$

The absolute efficiency for thermal ionization $\bar{\eta}_I(T)$, defined as (number of centers thermally ionized/unit time)/(number of centers excited/unit time), is

$$\bar{\eta}_R(T) = (1/\tau_I)(1/\tau_R + 1/\tau_N + 1/\tau_I)^{-1}. \quad (3)$$

In photoconductivity, it is often assumed that the temperature dependence of the photocurrent stimulated by illumination of fixed intensity and wavelength is the same as that of $\bar{\eta}_I(T)$, since the temperature range over which $\bar{\eta}_I(T)$ varies from near zero to near unity is generally small. This neglects temperature variations of the Schubweg, or mean distance traveled by the electron in the field direction before being trapped. The validity of this approximation depends upon the nature of the traps. Experimentally, one measures the photocurrent yield relative to the high-temperature yield, i.e., the quantity $\eta_I(T) = \bar{\eta}_I(T)/\bar{\eta}_I(T)/\bar{\eta}_I(\infty)$. Since $\tau_A \ll \tau_R \sim \tau_N$, $\bar{\eta}_I(T)$ is essentially unity at high temperatures so that we can assume $\bar{\eta}_I(T) = \eta_I(T)$. Consequently,

$$\eta_R(T) + \eta_I(T) = 1. \quad (4)$$

After pulsed optical excitation, the number of electrons in the excited state, and hence the luminescent intensity, decays exponentially with a time constant $\tau = \eta_R(1/\tau_R + 1/\tau_N)^{-1}$. Notice that none of these measurements of efficiency or lifetime permits one to distinguish τ_R from τ_N, so it is often assumed for simplicity that $1/\tau_N = 0$ and that τ_R equals the low-temperature radiative lifetime. In what follows, we will also make this assumption.

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

All of these processes are characterized by the branching ratio τ_R/τ_A and the activation energy Δ. Typical numbers for F centers are $\tau_R \sim 10^{-6}$ sec, $\tau_A \sim 10^{-13}$ sec and $\Delta \sim 0.1$ eV. Thus $(\tau_A/\tau_R)e^{\Delta/kT}$ becomes of order unity at $\approx 100°$K and changes by about an order of magnitude over a temperature interval of $\approx 20°$K. At lower temperatures, the excited F center predominantly decays by luminescence and at higher temperatures it is predominantly thermally ionized.

This simple model describes the behavior observed in most alkali-halide F centers, with some exceptions which can usually be put right by assuming a weak dependence of τ_R on T. The assumption that the luminescence and photoconductivity both originate from a single bound level implies that the lattice relaxation always deposits the electron in the same state, and that neither process depends on the wavelength of the exciting light. Experimentally, this is true in previously studied alkali halides, at least for excitation in the F band. (Excitation in the higher-energy K and L bands gives results which suggest that some of these states are not bound.) In the case of CsF, however, the photoconductivity is found to depend on the exciting wavelength in the F band, as will be described in Sec. III. To interpret this behavior it is useful to introduce an extension of the one-level model just described.

B. Two-Level Model

This model, diagrammed in Fig. 1(b), assumes that there are two bound levels in the relaxed lattice configuration and that the centers can be excited selectively to either. Each level is taken as having its own characteristic time for radiative decay to the ground state (we neglect nonradiative decay), and its own activation energy and attempt frequency for thermal ionization. The levels are denoted the $P_{1/2}$ and $P_{3/2}$ levels, anticipating the result that they are selectively excited in the $P_{1/2}$ and $P_{3/2}$ F-band components (see Ref. 1). The various characteristic times and energies are labeled in analogy with the one-level scheme by τ_{R1}, τ_{I1}, τ_{A1}, and Δ_1 and τ_{R3}, τ_{I3}, τ_{A3}, and Δ_3. The electron is also assumed capable of making transitions from the $P_{1/2}$ to the lower $P_{3/2}$ level at a spontaneous temperature-independent rate of $1/\tau_M$, with a thermally activated return rate $(1/\tau_M) \exp[-(\Delta_3 - \Delta_1)/kT]$. Lattice relaxation is assumed to accompany each of the transitions, the equilibrium lattice configuration differing depending upon whether the electron is in the $P_{1/2}$, $P_{3/2}$, or ground state.

One can write rate equations for this model. Let N_1 and N_3 be the populations of the $P_{1/2}$ and $P_{3/2}$ states, respectively, and let Q_1 and Q_3 be the rates at which centers are optically excited into the two states. Then,

assuming the $P_{3/2}$ level lies lower in energy,

$$\frac{dN_1}{dt} = -N_1\left(\frac{1}{\tau_{R1}} + \frac{1}{\tau_{I1}} + \frac{1}{\tau_M}\right)$$

$$+ N_3\left(\frac{1}{\tau_M}\exp\frac{-(\Delta_3-\Delta_1)}{kT}\right) + Q_1$$

and   (5)

$$\frac{dN_3}{dt} = -N_3\left(\frac{1}{\tau_{R3}} + \frac{1}{\tau_{I3}} + \frac{1}{\tau_M}\exp\frac{-(\Delta_3-\Delta_1)}{kT}\right)$$

$$+ \frac{N_1}{\tau_M} + Q_3.$$

It is straightforward to solve for N_1 and N_3 in the steady-state case $dN_1/dT = dN_3/dt = 0$, appropriate for dc luminescence or photoconductivity. The expressions take on a simpler form, however, after two approximations are made. First, reasonably, assume that the radiative lifetime τ_{R1} and τ_{R3} are long compared to the phonon-decay times τ_{A1}, τ_{A3}, and τ_M. Second, assume that $\tau_M \ll \tau_{I1}$ holds for temperatures reached in this experiment. These assumptions, whose validity is examined in Sec. IV, lead to the conclusion that in the case in which the excitation is to the $P_{3/2}$ state only, the $P_{1/2}$ and $P_{3/2}$ levels will be essentially in thermal equilibrium with each other (but not with the ground or conducting states), so that

$$N_1 \approx N_3 \exp[-(\Delta_3-\Delta_1)/kT]. \quad (6)$$

1. Photoconductivity in Two-Level Model

The quantum efficiency for photoconductivity η_p, defined as (number of centers ionized/unit time)/ (number of centers excited/unit time), is

$$\eta_p = \left(\frac{N_1}{\tau_{I1}} + \frac{N_3}{\tau_{I3}}\right) \Big/ \left[N_1\left(\frac{1}{\tau_{I1}} + \frac{1}{\tau_{R1}}\right)\right.$$

$$\left. + N_3\left(\frac{1}{\tau_{I3}} + \frac{1}{\tau_{R3}}\right)\right]. \quad (7)$$

Experimentally, it turns out that N_1/τ_{R1} is negligible compared to N_3/τ_{R3}, i.e., the number of radiative decays from the $P_{1/2}$ level is negligible. Using Eq. (6), one obtains the expression for photoconductivity excited in the $P_{3/2}$ level:

$$\eta_{p3}(T) = [1 + (\tau_{R3}/\tau_{A3} + \tau_{R3}/\tau_{A1})^{-1}e^{\Delta_3/kT}]^{-1}. \quad (8)$$

Under these assumptions, then, the two-level system excited in the $P_{3/2}$ level behaves as though there were a single activation energy Δ_3 and a branching ratio $(\tau_{R3}/\tau_{A3} + \tau_{R3}/\tau_{A1})$.

For excitation to the $P_{1/2}$ level, the expression for

the photoconductive efficiency is simplest for low temperatures, that is, temperatures for which $\eta_{P3}(T) \ll 1$. In this case the electron, once in the $P_{3/2}$ level, returns to the ground state with nearly unit probability. An electron excited into the $P_{1/2}$ level will either decay to the $P_{3/2}$ level (and thereafter to the ground state) with characteristic time τ_M or be ionized with characteristic time τ_{I1}. The radiative decay rate $1/\tau_{R1}$ is negligible compared to $1/\tau_M$. The photoconductive efficiency for excitation in the $P_{1/2}$ level, $\eta_{P1}(T)$, at low temperatures is then approximately equal to the quantity

$$\bar{\eta}_{P1}(T) = [1 + (\tau_{A1}/\tau_M)e^{\Delta_1/kT}]^{-1} \quad (9)$$

characterized by an activation energy Δ_1 and a branching ratio τ_M/τ_{A1}. We note that τ_M/τ_{A1} is expected to be of order unity, since it is the ratio of two phonon decay rates, which are of the order of lattice-vibration frequencies. This is in contrast to the branching ratio $(\tau_{R3}/\tau_{A1} + \tau_{R3}/\tau_{A3})$ obtained for $P_{3/2}$ excitation, which is of order 10^6.

At temperatures for which η_{P3} becomes appreciable, an electron, after being excited to the $P_{1/2}$ level, may be ionized directly or it may decay to the $P_{3/2}$ level, the ratio of the two probabilities being τ_M/τ_{I1}. Once in the $P_{3/2}$ level it has a subsequent ionization probability of η_{P3} so that the complete expression for the photoconductive efficiency for $P_{1/2}$ excitation at both high and low temperatures is

$$\eta_{P1}(T) = \bar{\eta}_{P1}(T) + [1 - \bar{\eta}_{P1}(T)]\eta_{P3}(T). \quad (10)$$

Thus at low temperatures we expect η_{P1} to be characterized by the smaller activation energy Δ_1 while at higher temperatures it is bounded by η_{P3}. If Δ_1 and Δ_3 differ substantially and the relative values of τ_M and τ_{A1} and τ_{A3} are favorable, one expects that at low temperatures the photoconductivity stimulated by wavelengths corresponding to the $P_{1/2}$ band will give a greater yield than that stimulated in the $P_{3/2}$ band.

2. Luminescence in Two-Level Model

This model contains the possibility of emission at two wavelengths, one corresponding to the $P_{3/2}$ level and one corresponding to the higher-energy $P_{1/2}$ level. It turns out experimentally, however, that at the temperatures of interest $\exp[(\Delta_3-\Delta_1)/kT] \gg 1$, so that for $P_{3/2}$ excitation $N_1 \ll N_3$ and consequently $N_1/\tau_{R1} \ll N_3/\tau_{R3}$, the luminescence from the $P_{3/2}$ level being the dominant process. For $P_{1/2}$ excitation, $\tau_M \ll \tau_{R1}$ by supposition and also experimentally, so that the electron nearly always either transfers to the $P_{3/2}$ level or, at higher temperatures, is thermally ionized. Consequently the only observed luminescence is due to radiative decay from the $P_{3/2}$ level to the ground state.

Let η_{L1} and η_{L3} be the quantum efficiencies for this luminescence for excitation in the $P_{1/2}$ and $P_{3/2}$ levels. Since the processes of thermal ionization and radiative

decay are assumed to be the only alternatives for the excited electron, one has

$$\eta_{L1}(T)+\eta_{P1}(T)=1$$

and

$$\eta_{L3}(T)+\eta_{P3}(T)=1.$$

(11)

The time decay for the luminescence following pulsed-light excitation can also be derived for this model. For $P_{3/2}$ excitation the decay is exponential with time constant $\tau_{R3}\eta_{L3}$. For $P_{1/2}$ excitation the electrons transfer into the $P_{3/2}$ level more quickly than can be resolved by available light sources, so that the decay time observed with $P_{1/2}$ excitation is again $\tau_{R3}\eta_{L3}$.

C. Schottky Ionization

Application of an electric field to the optically excited center increases the probability of ionization relative to that of return to the ground state.[3,4] For the temperatures and field strengths obtained in the experiments to be described the increase reflects a decrease in the thermal ionization time τ_I rather than field-induced tunneling. In the one-level model the electric field is taken as reducing the thermal activation energy Δ by an amount Δ' so that the thermal ionization time in the presence of field, $\tau_I(E)$, is related to the value in the absence of field, $\tau_I(0)$, by $\tau_I(E)=\tau_I(0)e^{-\Delta'/kT}$. In the two-level model both Δ_1 and Δ_3, and hence τ_{I1} and τ_{I3}, are presumably changed by the application of field.

In the experiments here the quantity actually measured is the field-induced change ΔI in the luminescent intensity I as a function of wavelength and temperature, where $\Delta I \ll I$ experimentally. In the one-level model, I is proportional to $\eta_R=(1+\tau_R/\tau_I)^{-1}$, so that for small changes Δ' in Δ, and hence small ΔI, $\Delta I/I^2 = -(\tau_R/\tau_A)(\Delta'/kT)e^{-\Delta/kT}$. In the two-level model the expressions are more complicated. For the low-temperature region, however, field-induced thermal ionization from the $P_{3/2}$ level is negligible (as can be shown experimentally by observing ΔI for $P_{3/2}$ excitation directly). Hence $\Delta I/I^2$ for $P_{1/2}$ level excitation is given by

$$\Delta I/I^2 = -(\tau_M/\tau_{A1})(\Delta'/kT)e^{-\Delta_1/kT}.$$

In the limited temperature region in which ΔI can be measured, $e^{-\Delta_1/kT}$ dominates the $1/kT$ term so that we expect that $|\Delta I/I^2|$ increases exponentially with temperature with activation energy Δ_1. We have neglected here again luminescence originating from recapture of thermally or field-ionized electrons by vacancies.

D. Optical Bleaching

Thermal ionization of optically excited F centers leads both to photoconductivity and also to a net destruction of F centers, as the freed electrons are usually trapped elsewhere than at a negative-ion vacancy. This destruction or "optical bleaching" is reflected in a decrease of the F-absorption-band optical density. The wavelength dependence of the optical bleaching is the same as that of the photoconductivity. The temperature dependence is similar to that of the photoconductivity, but may be influenced by the possibility of recapture of the ionized electrons by the vacancies.

Since at low temperatures photoconductivity from F centers has low efficiency, it is desirable to confirm that the photocurrent attributed to the F center is actually accompanied by optical bleaching of the F center. Otherwise it can happen that another species of center having a weak absorption band underlying the F band and having an efficient photoconductivity will give rise to a photocurrent that can be erroneously assigned to the F center. For the F center in CsF, for which the photoconductive response is found to have a wavelength dependence differing from that of the F-absorption band, such a confirmation is particularly necessary.

E. Ground-State Repopulation

The GSR technique is due to Fröhlich and Mahr[5] and to Park.[6] As used here, it involves illuminating a colored CsF specimen with a light pulse whose wavelength lies in the F band and whose duration and intensity are such that an appreciable fraction of the F centers are placed in their excited states. The absorption spectrum changes correspondingly, bands arising from transitions from the ground state being diminished and bands arising from transitions from the excited state to higher-energy states being created. At low temperatures these induced changes decay with a time constant characteristic of the return of the F center to its ground state. This is generally taken as being equal to the luminescent decay time, the lattice relaxation times being relatively short. For the F center in CsF, however, this is not the case, as will be seen in Sec. III.

In colored alkali halides the assignment of an optical-absorption band to any particular center is often ambiguous, the F center being only one of many centers which can be created by a coloring process. The GSR experiments are also useful in allowing one to associate with a common center those bands which both are simultaneously bleached by the light pulse and recover with the same characteristic time, e.g., the F band and the K band with the F center.

III. EXPERIMENTS

The experimental procedures and measurements of the luminescence, photoconductivity, Schottky ioniza-

[3] F. Lüty, Z. Physik **153**, 247 (1958).
[4] G. Spinolo and W. B. Fowler, Phys. Rev. **138**, A661 (1965).
[5] D. Fröhlich and H. Mahr, Phys. Rev. **141**, 692 (1966).
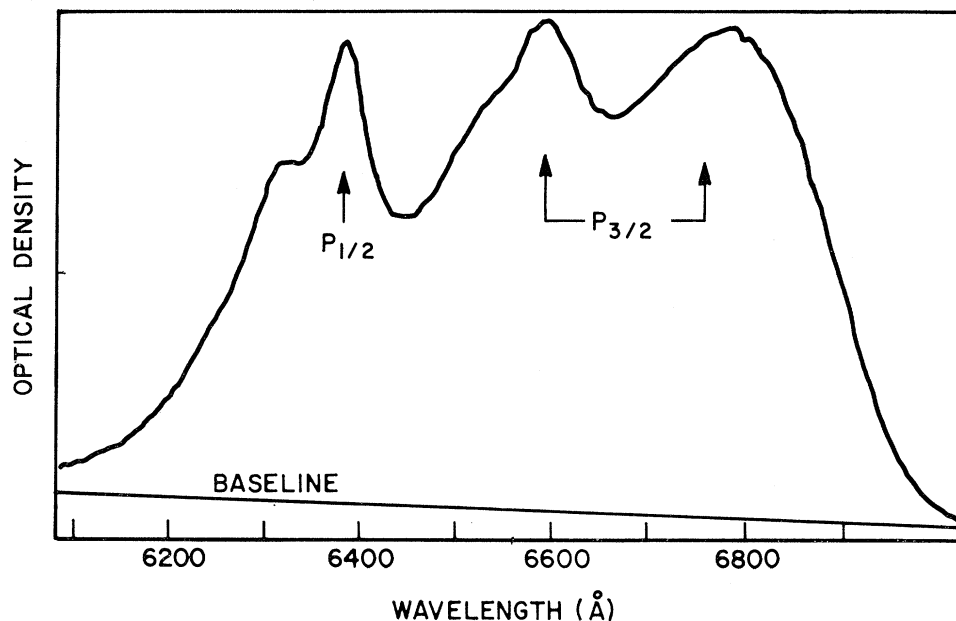[6] K. Park, Phys. Rev. **140**, A1735 (1965).

FIG. 2. F optical-absorption band of the CsF F center at 15°K. The assignment of the $P_{1/2}$ and $P_{3/2}$ levels are discussed in Ref. 1.
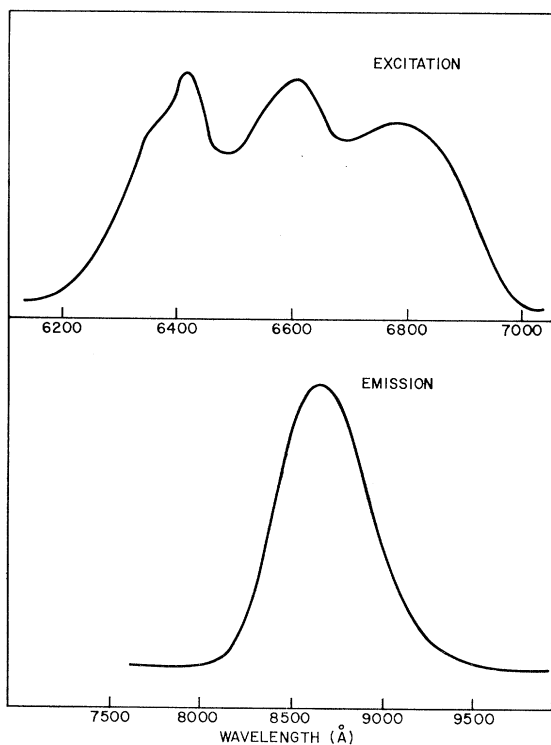

FIG. 3. 1.43-eV emission band and its excitation spectrum at 10°K. The spectra are uncorrected for monochromator and photomultiplier (S-1) response. The slit width of the exciting monochromator causes the apparent broadening of the phonon structure of the absorption band. Both signals are zero on the long-wavelength side.

tion, optical bleaching, and GSR investigations are described in this section. As none of the experiments was novel, the descriptions are brief. All measurements were complicated to some extent, however, by the difficulties of coloring and handling the deliquescent CsF. The treatment assumes some familiarity with the properties of the F center in optical absorption reported in Ref. 1.

A. Sample Preparation

Samples were cleaved from crystals of CsF supplied by the Harshaw Co. and Semi-Elements, Inc. In nearly all experiments the F centers were formed by x irradiation at liquid-nitrogen temperatures to avoid thermal bleaching and certain sample-dependent behavior encountered in other formation procedures, as discussed in Ref. 1. The optical-absorption spectra resulting have also been described in Ref. 1 and are shown in Fig. 2. We recall that the major absorption band resulting is the F band, which displays at temperatures below $\sim 250°K$ three well-resolved component peaks, centered at 1.94, 1.88, and 1.82 eV (640, 660, and 680 mμ, respectively) at the lowest temperatures. This triplet line shape results from a spin-orbit splitting of the excited P-like states into a higher-lying $P_{1/2}$ level, which gives rise to the high-energy F-band component, or $P_{1/2}$ band, and a lower-lying $P_{3/2}$ level which gives rise to the two lower-energy F-band components, or $P_{3/2}$ band. A dynamic Jahn-Teller effect causes the doublet appearance of the $P_{3/2}$ band. The additional fine structure of the high-energy and central peak result from resolved phonon transitions. There is also a weaker band at 2.17 eV (570 mμ) which the GSR experiments

described in this section indicate is due to a transition to a higher *F*-center level. This is called the *K* band in analogy to other alkali-halide *F* centers. Upon occasion, other sample-dependent bands occur which can play a role in photoconductivity and luminescent behavior of the sample, so that it is necessary to exercise some care in interpreting experimental results.

B. Luminescence

Colored CsF possesses a strong luminescence band which at low temperatures peaks at 1.43 eV (865 mμ) with a width of 0.1 eV. Both the Stokes shift and the width are small by *F*-center standards. This emission band and its excitation spectrum are shown in Fig. 3 for a sample at 10°K colored by x irradiation *in situ*

FIG. 5. 1.43-eV emission-band luminescence pulse resulting from pulsed-laser excitation at *F*-band wavelengths. The curves are tracings from the oscilloscope photographs. (a) Ruby-laser pulse for (b). (b) 1.43-eV emission pulse at 77°K. (c) Ruby-laser pulse for (d). (d) 1.43-eV emission pulse at 10°K. All signals are initially zero at the left.
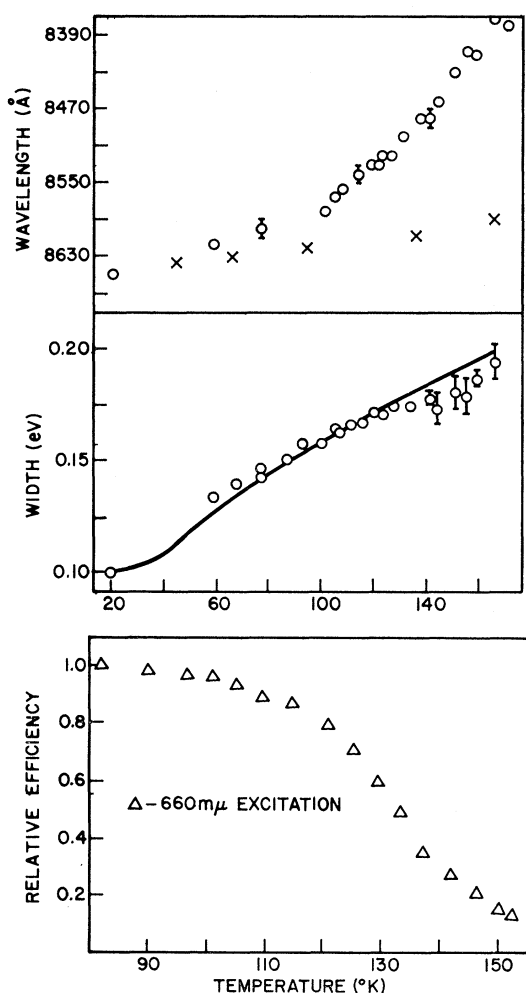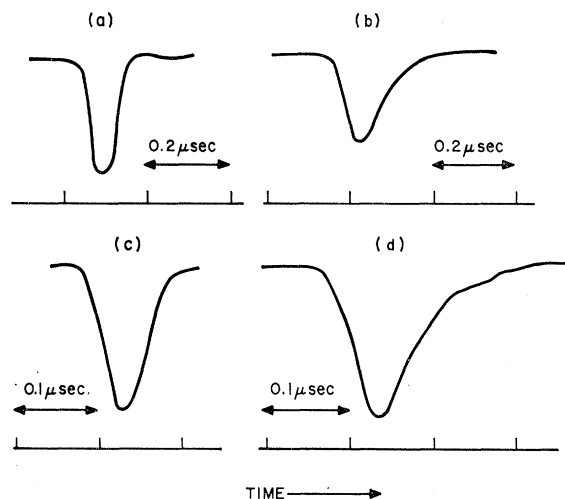

FIG. 4. Temperature dependence of the 1.43-eV emission-band position, breadth, and intensity. The position is taken as the average of the two half-intensity points rather than the peak position. The solid-line fit to the temperature dependence of the breadth is discussed in text. The crosses indicate the apparent shift resulting from the broadening and the E^3 factor in the transition probability.

at liquid-nitrogen temperatures, $\approx 77°$K. Note the characteristic three peaks and the substructure of the excitation spectrum which match those of the *F* band in absorption. Similar spectra were found for both Harshaw and Semi-Elements samples over a concentration range of 10^{15} to 7×10^{16} cm^{-3}. A crude check of the extent of polarized emission caused by [100] polarized exciting light showed equal emitted intensities to within 10% for polarizations parallel and perpendicular to that of the exciting light.

When the crystal is warmed above 10°K, this emission band broadens, and shifts to higher energies (unusual for *F* centers) as shown in Fig. 4. The relative efficiency of this luminescence, defined as the yield relative to the yield at 77°K, is also shown versus temperature in Fig. 4. The yield, as measured by the area under the emission band, is essentially constant below these temperatures. The absolute quantum efficiency, defined as the number of centers decaying by emission in this band compared to the number excited, was measured at 77°K by relating the intensity of the emitted light to that of the exciting light in a procedure which sampled both with the same S-1 response photomultiplier tube and made corrections for tube sensitivity, solid angle factors, filter and window losses, and sample transmission. The resulting efficiency was calculated to be 0.9 ± 0.2, indicating that most of the excited centers contribute to the 1.43-eV emission band at low temperatures.

The lifetime of this luminescence was investigated both by using a fast spark and a *Q*-switched laser as exciting sources. The lifetime is unusually short, as shown in Fig. 5, where both the 30-nsec laser pulse and the resulting luminescence pulse are shown. To extract

the lifetime one may either unfold the luminescence signal assuming an initial Gaussian laser pulse or measure the decay of the pulse tail in a time region in which the laser pulse has essentially ceased. Both numbers agree with a lifetime of 50±10 nsec for both helium (10°K) and nitrogen (77°K) temperatures. An upper limit of 0.1 μsec, consistent with this value, was obtained using the weaker slower (0.1 μsec) spark source.

Two other luminescent processes were observed, both almost certainly extrinsic. One resulted in a broad weak luminescence band centered at about 1.25 eV (1.0 μ), obscured under the tail of the 1.43-eV band except at the lowest temperatures. The luminescent lifetime for this band was found to be 2 μsec at helium temperature, as compared with the radiative lifetime of 50 nsec for most of the F centers. The excitation spectrum of this band at 10°K is shown in Fig. 6. Note that the band could be excited in the K band and to a lesser extent in the $P_{1/2}$ band, but not at all in the $P_{3/2}$ band. Considering the long lifetime and the excitation spectrum which does not agree with the absorption band shape, it is probable that the 1.25-eV band is a dirt effect, involving energy transfer from a small percentage of the F centers to some other center or impurity. As will be seen, however, the excitation spectrum showing different $P_{1/2}$ and $P_{3/2}$ band response is a common feature of several of the experiments.

Another observed luminescent process which is obviously extrinsic is a *blue* emission visually observed in an x-rayed sample illuminated by *red* light of F-band wavelength. This emission is accompanied by bleaching of the F centers and results most probably from the

recombination of electrons, freed by thermal ionization or other means in the illumination, with hole centers formed in the irradiation. A luminescence of similar visual appearance results as a thermoluminescence in warming the x-rayed samples to room temperature in the dark, again with a loss of F centers. The shape of the emission band was not measured, but the band extends from the blue end of the visible spectrum into the near ultraviolet. The low-temperature excitation spectrum in the F-band region is similar to that of the 1.25-eV emission band, showing again response in the K band and $P_{1/2}$ band but not the $P_{3/2}$ band.

C. Photoconductivity

Photocurrent response was measured as a function of excitation wavelength and temperature over the range 80–200°K, using apparatus and procedures similar to those of Inchauspé.[7] The principal difference, and the biggest difficulty, was that the crystal had to be colored by x irradiation while immersed in liquid nitrogen and then mounted in the measuring cryostat in a dry atmosphere while cold. X irradiation *in situ* caused large spurious "thermal glow" currents.

The sample was held between two blocking electrodes and was illuminated through one of the electrodes, made of thin wire mesh and 0.001-in. Mylar film. The other electrode was in contact with a liquid-nitrogen bath through an exchange-gas can. The photocurrent was measured with a vibrating-reed electrometer using a 20-sec illumination period. The photocurrents were kept below 10^{-13} A, neutral optical filters of known attenuation being used for this purpose when necessary, and the voltage was reversed between readings to avoid space-charge effects. The optical density of the sample was kept small so that the number of photons absorbed was proportional to the absorption constant.

Experimental runs involved monitoring the photocurrent at a particular wavelength while the sample was warmed from liquid-nitrogen temperature, or alternately, monitoring the photocurrent for fixed temperatures over a range of exciting wavelengths. Runs were made on two separate Harshaw samples. The photocurrents for three different excitation wavelengths and at various temperatures for one sample are shown in Fig. 7. The currents show a saturation at high temperatures, presumably as the result of the thermal-ionization probability approaching unity, and the currents are normalized to the saturation currents. The most striking feature is the very different response in different parts of the F band at low temperatures. The spectral response for this sample at 84°K, shown in Fig. 8, demonstrates this explicity, the photocurrent excited in the K and $P_{1/2}$ bands being at least an order of magnitude larger than the photocurrent excited in the $P_{3/2}$ band. At high temperatures ($\approx$190°K) the excitation spectrum for photoconductivity is qualita-
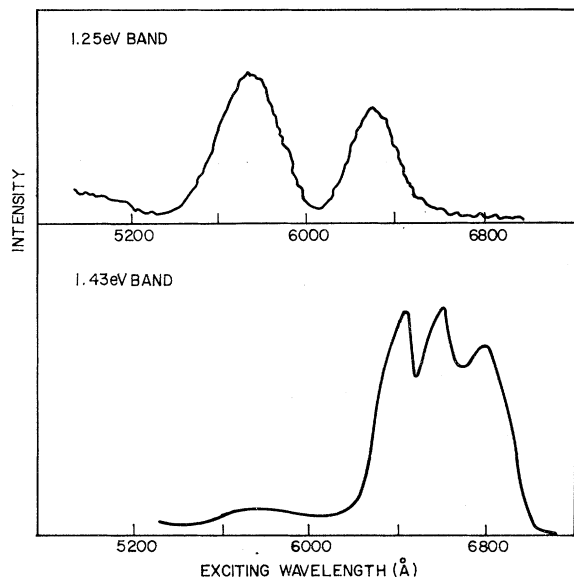

FIG. 6. Excitation spectrum of the 1.25-eV emission band. The excitation spectrum for the 1.43-eV band is shown for comparison. Curves are uncorrected for monochromator response.

[7] N. Inschauspé, Phys. Rev. 106, 898 (1957).

tively the same as the absorption spectrum, although the measurements were not very accurate. The second sample produced similar results, except that corrections for optical bleaching of the centers during the runs were required for this more lightly colored sample.

D. Optical Bleaching

Investigations of the optical bleaching of the CsF *F* center were conducted for temperatures at and above that of liquid nitrogen. The absorption spectrum of a sample mounted and x-rayed at 77°K in a standard
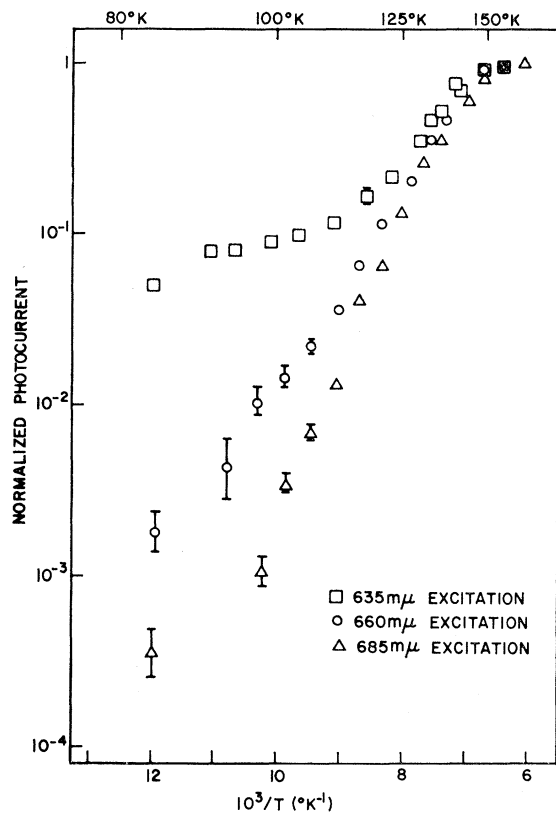

FIG. 7. Photocurrent versus temperature for three wavelengths of exciting light in the *F* band.

optical cryostat would be measured initially in a Cary 14R spectrophotometer. The sample would then be exposed to near-monochromatic light of a desired wavelength for some minutes, by simply opening wide the Cary slits, without moving the cryostat. Following this the absorption spectrum would be measured again, and any changes noted.

For moderately high temperatures, e.g., 200°K, the *F* band could be bleached with reasonable efficiency by wavelengths lying anywhere in the *F* or *K* bands. For lower temperatures, around 77°K, the bleaching was found to be efficient in the *K* band and $P_{1/2}$ band but not in the $P_{3/2}$ band. The effect is quite marked;
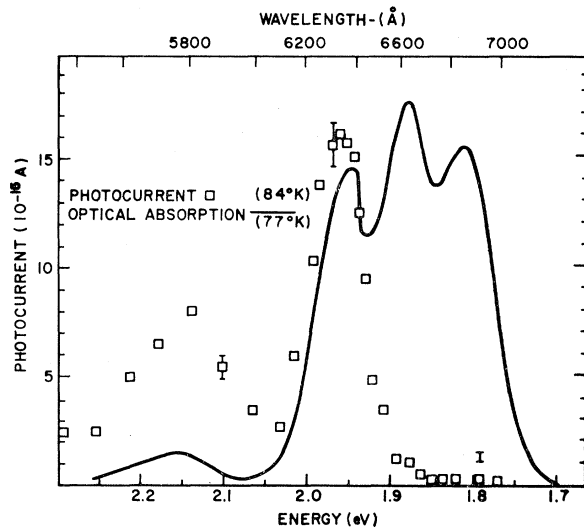

FIG. 8. Wavelength dependence of the photocurrent at $\approx 84°K$. Also shown is the optical-absorption spectrum at 77°K.

for example, in a Semi-Elements sample at $\approx 77°K$ about one-half of the *F*-band optical density could be removed by a $\frac{1}{2}$-h exposure to $P_{1/2}$ wavelengths, while a similar exposure to $P_{3/2}$ wavelengths gave a change of less than 2%. Harshaw samples showed a similar $P_{1/2}-P_{3/2}$ difference, although the bleaching rate was about three times slower than in the Semi-Elements samples. The slower rate may be the result of the different available traps in the crystals as the bleaching rate depends not only on the thermal-ionization efficiency but also on the recombination rate of freed electrons with the vacancies.

E. Schottky Ionization

As described in Sec. II, the Schottky ionization experiments investigate the electric-field-induced increase in thermal ionization by measuring the complementary decrease in luminescence. The relative ease and sensitivity of optical measurements compared to those of photoconductivity makes this technique a useful probe of the thermal ionization even to low temperatures. The ac-field-induced changes ΔI in the luminescent intensity I of one part in 10^5 can be observed using phase-sensitive detection. Techniques and equipment for such measurements have been developed by Bogan,[8] and the following experiment was done in close collaboration with him.

A Semi-Elements sample was x irradiated to an optical density of ≈ 0.3 at 77°K *in situ* in the electric field cryostat. The sample was cooled to helium temperatures (10°K) and was then warmed slowly to liquid-nitrogen temperatures, the values of I and ΔI being recorded as the exciting wavelength was swept

[8] L. D. Bogan, Ph.D. thesis, Cornell University 1968 (unpublished); L. D. Bogan and D. B. Fitchen (unpublished).
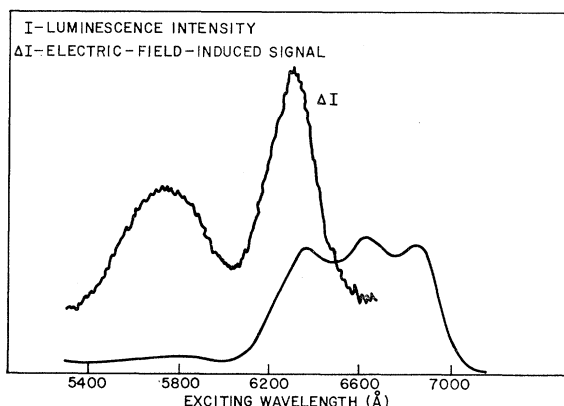
FIG. 9. Schottky ionization at 72°K. Wavelength dependence of the luminescence intensity I and the electric-field-induced changes ΔI in I. Both ΔI and I are zero on the long-wavelength side.

over the F and K bands at successively higher temperatures. I and ΔI for such a scan at 72°K and for a field of ≈ 25 kV/cm are shown in Fig. 9. Here again the K and $P_{1/2}$ band excitations both give a response, while the $P_{3/2}$ band does not.

The quantity $\Delta I/I^2$ for the peak responses in the $P_{1/2}$ and K bands is shown versus temperature in Fig. 10. This quantity rises approximately exponentially for temperatures up to $\approx 60°$K and then levels off. Bogan has shown in a previous experiment[8] that
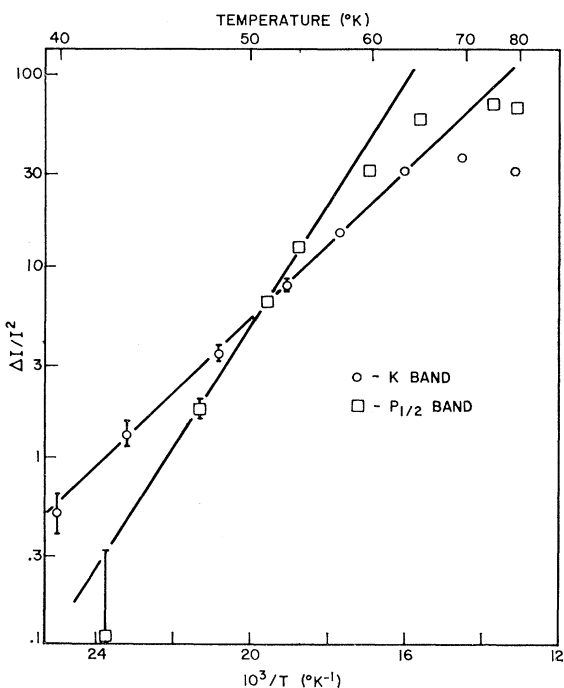

FIG. 10. $\Delta I/I^2$ versus temperature for the Schottky ionization for both $P_{1/2}$ and K-band excitation. The values of $\Delta I/I^2$ for the K band have been multiplied by 0.12.

the field-induced ionization at higher temperatures for both $P_{1/2}$ and $P_{3/2}$ excitation begins to increase again at temperatures around 120°K and climbs rapidly, as one would expect from the photoconductivity.

Note that in the spectral response, both in Fig. 9 and in the 1.25-eV emission band excitation spectrum of Fig. 6, the peak of the $P_{1/2}$ response is not at the peak of the $P_{1/2}$ absorption but is about 100 Å to shorter wavelengths. This displacement does not depend on temperature in the Schottky ionization experiments, nor do the individual shapes of the $P_{1/2}$ or K band appear to change with temperature, although the relative strengths of the two do of course change, the K band being the stronger of the two at lower temperatures and the weaker at higher temperatures.

F. GSR Experiments

In earlier work of Fröhlich and Mahr[5] a GSR experiment was carried out on an electrolytically colored CsF sample, using the Q-switched ruby-laser pumping light at 6943 Å in the low-energy tail of the $P_{3/2}$ component of the F band to pump a sizable fraction of the F centers into the excited state. The decrease in F-band absorption caused by this temporary bleaching was found to recover with a characteristic time of 1.1 μsec. As this time was at odds with our measured luminescent lifetime of 50 nsec in x-ray-colored samples, it was decided to repeat the Fröhlich-Mahr experiment using the x-rayed samples.

Two separate runs on x-rayed specimens were conducted, using the original equipment of Fröhlich and Mahr. Details of the method can be found in their paper.[5] Briefly, the transmission of the sample is monitored at a desired wavelength, usually in the F or K bands using a system of monochromators and a white-light source. The change in the transmitted intensity of the monitoring light caused by the laser pulse is detected by a photomultiplier and the time decay of the laser-induced signal is recorded photographically on an oscilloscope. One may also measure the luminescent lifetime in this arrangement by blocking the white-light source and monitoring the emission wavelength of 865 mμ, recording the time decay of the laser-induced emission with the same electronics and optics as in the transmission.

Examples of the data are shown in Fig. 11 for a Harshaw sample at 10°K with a peak F-band optical density of 0.8. The curves (a) and (b) are for monitoring wavelengths of 570 and 650 mμ, respectively, and show a recovery time of order 1 μsec, while (d) and (e) show the much faster 1.43-eV emission and the incident laser pulse. Note that the 570-mμ signal shows an initial sharp spike due to pickup of the scattered light from the laser. In Fig. 12 we show a semilog plot of the change in transmission versus time for the curves (a) and (b). The theoretical time decay of the induced transmission signal is not strictly exponential, but it is
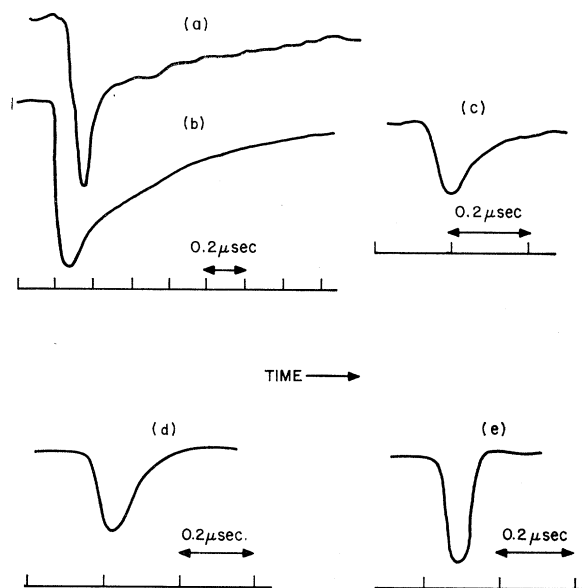
FIG. 11. GSR data. Curves (a) and (b) show variation in transmission with time for monitoring wavelengths of (a) 570 mμ (*K* band) and (b) 650 mμ (*F* band), both at $\approx 10°$K. Curve (c) shows the transmission versus time at 650 mμ at 77°K, (d) the 1.43-eV emission decay, and (e) the laser pulse which stimulates the emission and transmission changes. The initial sharp spike of (a) is due to scattered laser light.
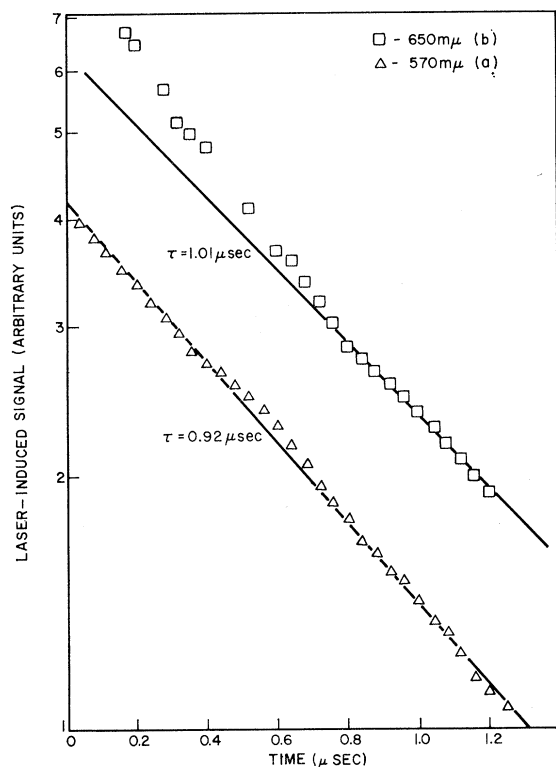

FIG. 12. Semilog plot of the variation in transmission versus time for curves (a) and (b) of Fig. 11.

nearly so for small changes in the transmission, such as in the *K*-band signal or the latter stages in time of the *F*-band signal, and the time constant is the characteristic GSR time.

The salient features of the data on the x-rayed samples are:

(a) The *K*-band absorption is decreased by pumping of the *F* centers and recovers with the same characteristic time as do the three peaks of the *F* band. This is the most concrete evidence for the identification of the *K* band as an *F*-center transition which was assumed in Ref. 1.

(b) This recovery time is 1.00±0.05 μsec at temperatures below 40°K, much longer than the luminescent lifetime of 50 nsec and in agreement with the Mahr-Fröhlich value.

(c) At temperatures above 40°K the GSR time decreases until at nitrogen temperature it has a value comparable to the 50-nsec luminescence lifetime.

In Fig. 13 we reproduce the original Mahr-Fröhlich data showing the GSR lifetime temperature dependence for the electrolytically colored sample. The behavior is in accord with that which we have observed in the x-rayed samples.

IV. DATA ANALYSIS ON TWO-LEVEL MODEL

The data presented in the previous section show that the behavior of the optically excited *F* center in CsF is unusual for an *F* center. In this section we attempt to fit these data into the framework of the two-level model discussed in Sec. II, reserving for Sec. V a discussion of the physical nature of the states involved. In particular we will leave till Sec. V any comment on the curious GSR results.

The two-level model deals with a correlation of the efficiency and lifetimes of the luminescence and photoconductive processes. Its application to the *F* center in CsF is straightforward, starting with the identification of the 1.43-eV emission band as the major luminescent process in this *F* center. This band has a low-temperature quantum efficiency near unity and an excitation spectrum which duplicates the *F* band. The temperature dependence of the efficiency is complementary to that of the photoconductivity, indicating that the only two important fates for the excited *F* center are thermal ionization or radiative decay, the latter process contributing a photon to the 1.43-eV emission band. This band is therefore taken as corresponding to the radiative decay from the $P_{3/2}$ level to the relaxed ground state in the two-level model.

The photoconductivity, Schottky ionization, optical bleaching, and the two extrinsic luminescent processes all show excitation spectra which make it clear that the thermal-ionization probability is not the same for centers excited in the $P_{1/2}$ and $P_{3/2}$ bands, a result anticipated in Sec. II. We associate the $P_{1/2}$ and $P_{3/2}$
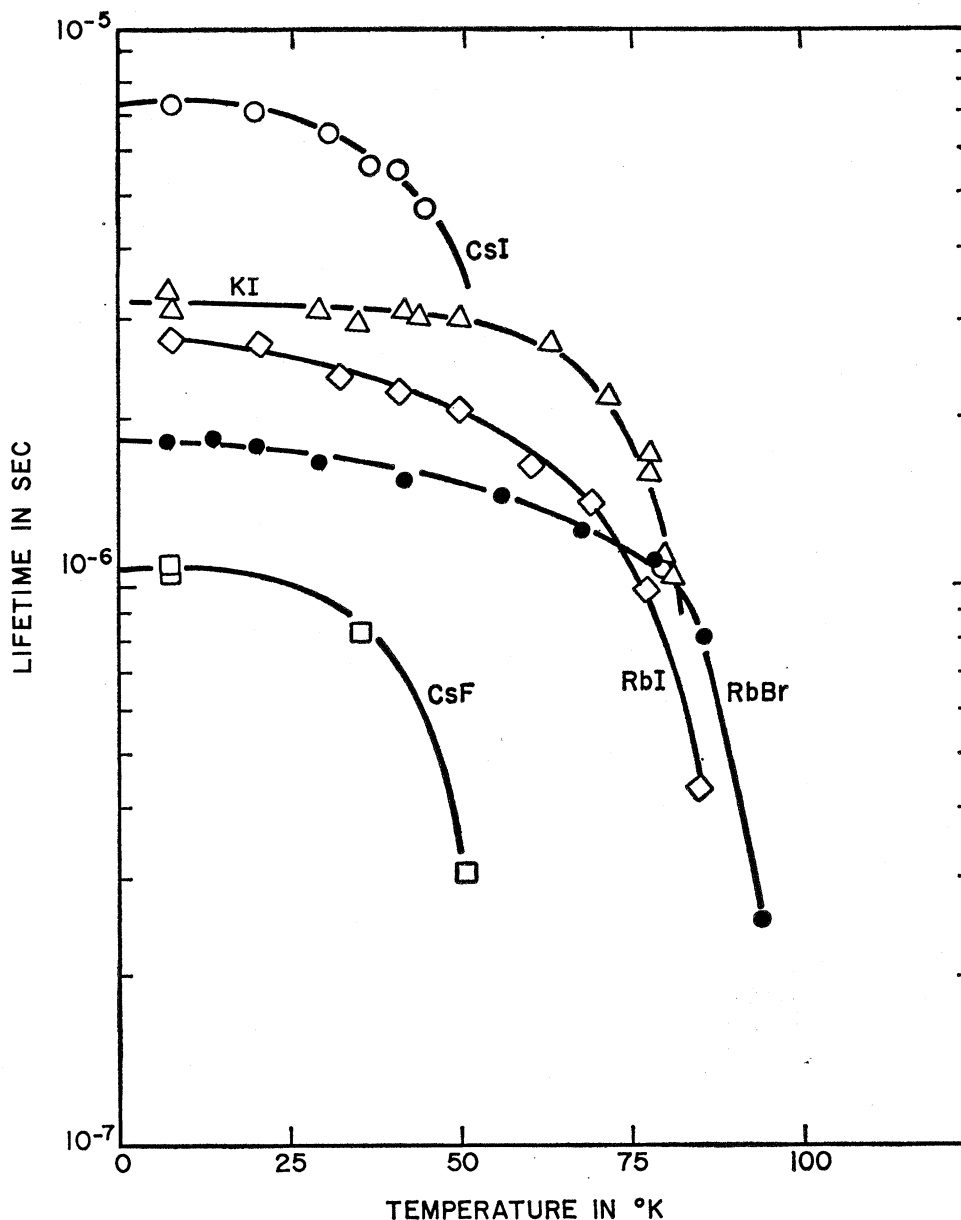
FIG. 13. GSR time versus temperature for CsF and other alkali-halide F centers after Ref. 5.

levels of the two-level model with their namesake absorption bands. As described in Sec. II, this model can lead to excitation spectra of the general sort observed at both lower and higher temperatures. The question is whether one can find a set of characteristic times and activation energies which will quantitatively account for all the temperature-dependent aspects.

According to the analysis of Sec. II, the efficiency of photoconductivity excited in the $P_{3/2}$ level should be characteristic of a simple single-level thermal activation process. The photocurrent yield plotted in Fig. 7 has the general appearance that is expected for this process. We assume that the normalized currents I/I_{max} shown in Fig. 7 are equal to the thermal-ionization probability, neglecting as before temperature dependence of the Schubweg, and plot in Fig. 14 $\log_{10}[(I_{max}/I)-1]$ versus $1/T$ for the $P_{3/2}$ and $P_{1/2}$ (635 mμ) excitations. According to Eq. (8) this will give a straight line, the slope giving the activation energy and the intercept at $1/T=0$ giving the branching ratio. In Fig. 14 it can be seen that the photoconductive yield for excitation in the $P_{3/2}$ band is well described by such a relation over more than two orders of magnitude in I/I_{max}. The activation energy is $\Delta_3=0.19\pm0.02$ eV
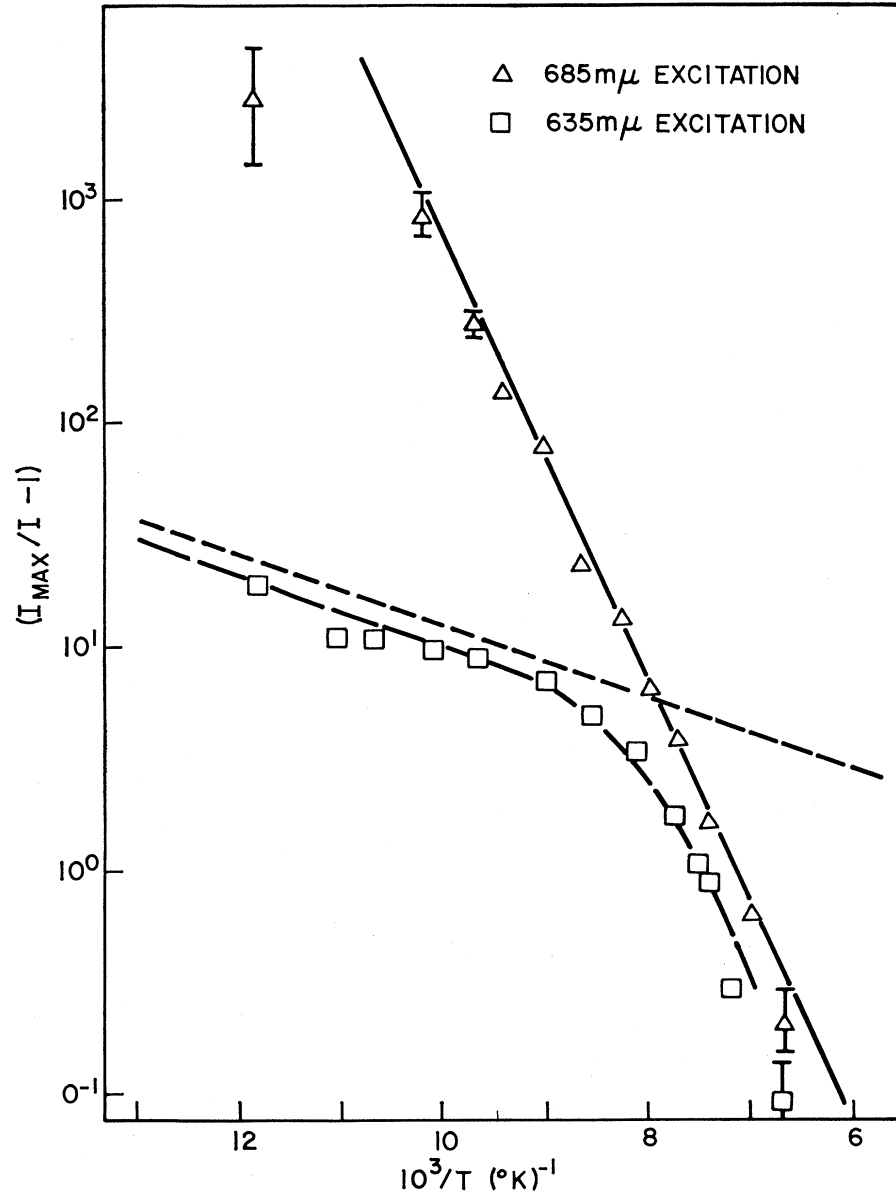
FIG. 14. Photocurrent data of Fig. 7 plotted as $\ln(I_{max}/I-1)$. The theoretical fits of the solid and broken lines are described in the text.

and the branching ratio is

$$\frac{\tau_{R3}}{\tau_{A3}} + \frac{\tau_{R3}}{\tau_{A1}} = (5.7_{-3.2}^{+6.8}) \times 10^5.$$

The quantities are obtained by making the best straight-line fit by eye, while the uncertainties are values which give a noticeably worse fit to the data. The fit is shown by the solid line in Fig. 14. Using the value $\tau_{R3} = 50$ nsec corresponding to the 1.43-eV emission-band lifetime, appropriate values for the τ_A's are of the order of 10^{-13} sec.

The situation for the $P_{1/2}$ excited photoconductivity is not as satisfactory. From Eq. (9), we expect that at lower temperatures the values of I/I_{max} would conform

again to a simple thermal-activation picture characterized by activation energy Δ_1 and branching ratio τ_M/τ_{A1}. The criterion for this limiting case is that the thermal-ionization probability from the $P_{3/2}$ level be small compared to that from the $P_{1/2}$ level, a condition satisfied for temperatures below $\approx 110°$K. The values of I/I_{max} for $P_{1/2}$ excitation between these temperatures and the lowest temperature reached, $\approx 85°$K change by only a factor of about 2.5, so that it is difficult to achieve a definitive fit. The slope of the dashed straight line in Fig. 14, 0.03 eV, appears to be a reasonable upper bound on the activation energy, and the intercept at $1/T = 0$ corresponds to $\tau_M/\tau_{A1} = 3.2$, a number of order unity as anticipated in Sec. II. The dashed line in Fig. 14 is constructed from the full expression for η_{P1}, Eq. (10),

using the parameters $\Delta_1 = 0.03$ eV, $\tau_M/\tau_{A1} = 3.0$, $\Delta_3 = 0.19$ eV, and $(\tau_{R3}/\tau_{A3} + \tau_{R3}/\tau_{A1}) = 10^6$. The different choice of branching ratio for the $P_{3/2}$ process is required by the fact that the $P_{1/2}$ and $P_{3/2}$ data at high temperatures are slightly offset, probably as a result of experimental inaccuracies in the determination of the photocurrents at the higher temperatures. Note that if the values of η_{P1} at low temperatures, which are a measure of τ_M/τ_{I1}, are extrapolated to the maximum temperatures reached in the experiments, they are of order 25%, which supports the approximation of τ_{I1} large compared to τ_M leading to Eq. (8). The exponential dependence of $1/\eta_{P3} - 1$ on $1/T$ predicted by (8) also seems to be fulfilled.

Based on the photoconductivity results down to nitrogen temperatures, then, we have achieved a fit to the data on the two-level model using activation energies of $\Delta_3 = 0.19$ eV and $\Delta_1 = 0.03$ eV. The latter number could perhaps be made smaller and still allow a reasonable fit of the data, but probably not larger. If one attempts to force a fit using $\Delta_1 = 0$, i.e., a constant probability for thermal ionization at low temperatures, then τ_{A1}/τ_M adjusts to 15–20, i.e., the photoconductive efficiency at low temperatures is about 5%.

The Schottky ionization results disagree, however, with the numbers derived from the photoconductivity. As discussed in Sec. II, at low temperatures one expects the luminescence quenching rate in the $P_{1/2}$ level to increase exponentially with increasing temperature, $\Delta I/I^2$ being proportional to $e^{-\Delta_1/kT}$. A plot of $\ln(\Delta I/I^2)$ is shown in Fig. 10 and gives, in fact, an approximately exponential increase up to $\approx 60°$K. The slope, however, corresponds to an activation energy of 0.06 eV, twice that deduced as an upper bound from the photoconductivity at the somewhat higher temperatures between 85 and 100°K. A second puzzling feature is that above the 60°K temperature the value of $\Delta I/I^2$ levels off to an approximately temperature-independent value which it maintains up to the $\approx 75°$K reached in these experiments. (Previous experiments of Bogan[8] have shown that the Schottky ionization rate begins increasing again at $\approx 120°$K and increases exponentially thereafter at a rate governed by a thermal-activation energy of 0.18 eV, in good agreement with the value of Δ_3 deduced from the photoconductivity.) Since the value of $e^{-0.06\,\mathrm{eV}/kT}$ changes from 10^{-5} to 10^{-4} over this temperature range, it is hard to understand a temperature-independent field-induced ionization. If the prefactor of the exponential were of order 10^4, such an effect could occur, but this would imply that ΔI approaches I, i.e., nearly complete field ionization, while experimentally $\Delta I \ll I^2$.

Although the photoconductivity and Schottky ionization data are not inconsistent, it does not seem possible to fit them both with a single two-level model, barring *ad hoc* assumptions about a temperature dependence for τ_M or other parameters. It may well be that the lattice relaxation process is in reality too complex to be described by the simple one- and two-level models. Alternately, the discrepancy may result from neglect of Schubweg temperature dependence and F-luminescence contributions from electron-vacancy recombination, particularly if F centers or vacancies are involved in trapping of the freed electrons.[9] Nonetheless, it is apparent that although the final state reached ln lattice relaxation is the same for both $P_{3/2}$ and $P_{1/2}$ excitation, for the latter there is at least one intermediate stage of the lattice relaxation. This stage lasts sufficiently long that the thermal-ionization probability during this stage is comparable to the probability of continued lattice relaxation. The spin-orbit splitting of the P-like states is of course involved in this behavior and some speculations about the physical nature of the processes involved will be presented in Sec. V.

As regards the optical bleaching and extrinsic luminescence bands, their excitation spectra can be understood on the two-level hypothesis. It is clear that the wavelength and temperature dependences of the optical bleaching are required by those of the photoconductivity, and that they are additional evidence that the low-temperature photocurrents observed actually come from the F center. The blue emission, as mentioned in Sec. III, could well be recombination radiation of the thermally freed electrons. The 1.25-eV emission, on the other hand, probably represents a process of energy transfer to a nearby impurity at a small fraction of the centers. At low temperatures the ratio of intensities for the 1.25-eV luminescence excited in the K and $P_{1/2}$ bands is of order unity (Fig. 6) whereas the Schottky ionization results of Fig. 10 suggest that at these temperatures only the K band would give appreciable thermal ionization, indicating that the 1.25-eV emission is not characteristic of the unperturbed centers.

To close this section we deal briefly with the thermal broadening and shift of the 1.43-eV emission band. The temperature dependence of the width W can be fit by the standard formula $W(T) = W(0) \coth(\hbar\Omega/2kT)$, which is based on the assumption of linear coupling of the transition to phonons of a single effective frequency Ω. A fit of this formula to the data of Fig. 4 gives the value $\hbar\Omega = 59 \pm 3$ cm^{-1}. The fit using $\hbar\Omega = 59$ cm^{-1} is shown by the solid line in Fig. 4, and the uncertainty is given as extending to values of $\hbar\Omega$ which give a noticeably worse fit to the experimental data.

The apparent blue shift of the emission band with increasing temperature is not understood in detail. Concerning it, note first that the hydrostatic pressure shift of the optical-absorption band is nearly zero, suggesting that the lattice thermal expansion should be relatively ineffective in shifting the band energies. In this case also, however, assuming similarities be-

[9] H. Fedders, M. Hunger, and F. Lüty, J. Phys. Chem. Solids 22, 299 (1961).

tween the properties of the relaxed and unrelaxed
states may be a dubious procedure. Also note that an
apparent blue shift of the emission band arises just
from the (energy)³ factor of the radiative density of
states as a result of the thermal broadening of the band.
The crosses shown in Fig. 4 indicate the shift arising
from this factor for the observed broadening, taking
again the point midway between the two half-intensity
energies as the band position. About 15% of the shift
can be ascribed to this source.

V. NATURE OF RELAXED STATES

An understanding of the physical nature of the
relaxed excited and ground states, and of the lumines-
cent transitions between them, hinges upon an as yet
unachieved understanding of the bottleneck in the
GSR experiments. These experiments show the follow-
ing: The majority of the centers emit photons of energy
corresponding to the 1.43-eV emission band after ab-
sorbing a photon of energy 1.79 eV, corresponding to
the ruby-laser frequency in the extreme red tail of the
F band. The energy consumed by lattice relaxation in
the cycle is 0.36 eV/center. The lattice relaxation that
follows absorption of the photon occurs in $\lesssim 10$ nsec,
since for pulsed-laser excitation no delay is observed
between the exciting light pulse and the onset of the
luminescence to within this time resolution. Since the
luminescent lifetime at low temperatures is 50 nsec,
the majority of the excited centers are at most 0.36
eV above the ground state within ≈ 100 nsec after
excitation. The time required for the *F*-absorption-band
recovery, however, is 1.0 μsec at helium temperatures,
so one is forced to conclude that there exists a metasta-
ble state or position for the *F*-center electron *after the
emission*, of about 1.0-μsec lifetime, much longer than
the nominal 10^{-10}–10^{-11} sec usually expected for lattice
relaxation. This metastable state is at an energy above
the ground state of no more than 0.36 eV, and probably
less than that depending on how much energy is con-
sumed in the intervening lattice relaxations.

If it were not for this peculiar behavior, one could
proceed in the usual fashion by assuming that the
1.43-eV emission band is the $P \rightarrow S$ transition com-
plementary to the $S \rightarrow P$ absorption band and go on
to discuss the nature of the relaxed states in light of
the properties of the luminescence and photoconduc-
tivity on this basis. The bottleneck in the lattice
relaxation after the radiative transition, however, has
no obvious, plausible explanation in this scheme.
Nonetheless it is still of some interest to examine the
results of such a procedure and this is done in what
follows. In the process the possible source of the two-
level behavior of the lattice relaxation will also be
discussed. Speculations on the possible nature of the
bottleneck form the subject of the final portion of this
section.

A. "Standard Interpretation"

As pointed out in Sec. IV, the quantum efficiency,
temperature dependence, and excitation spectra of the
1.43-eV emission band are what would be expected of
a $P \rightarrow S$ transition of the usual type. In what follows
we make this assumption, setting aside for the moment
the question of the GSR bottleneck.

The properties of the 1.43-eV emission band may be
compared to those expected on the diffuse-state model.[10]
This model depicts the relaxed excited state as a degen-
erate set of three relatively diffuse *P*-like states, spread
over a large radius surrounding the halide vacancy.
These states are treated as hydrogenic with appro-
priate corrections for the dielectric constant, somewhat
like those of a donor in a semiconductor. The relaxed
ground state is depicted as relatively compact, con-
fined largely to the halide vacancy. The relaxed-lattice
ion configuration is cubic. This model accounts for
several properties of the *F*-center luminescence in the
commonly studied alkali halides including (a) the
relatively low oscillator strength and consequent long
radiative lifetime of ~ 1 μsec, which contrasts to the
absorption oscillator strength of order unity, (b) the
insensitivity of these lifetimes to the presence of a
neighboring foreign alkali atom (*F*A center),[11] and (c)
the weak effect of uniaxial stress on the luminescence,
suggesting a *P* state splitting ~ 100 times smaller than
for the unrelaxed state for similar stresses.[12] (Recent
experiments on electric field effects[8] suggest that the
relaxed 2*S* state may be nearly degenerate with the
2*P* states and that its influence cannot be neglected.
The situation with regard to CsF is discussed in Ref. 8.)

Certainly it is reasonable that the relaxed wave
functions should differ substantially from the unrelaxed,
since typically half the photon energy is consumed in
lattice relaxation. The 1.43-eV emission band of the
CsF *F* center, however, has a Stokes shift of 0.45 eV,
about a quarter of the absorption photon energy, so
one might anticipate a less distorted set of wave func-
tions than for other *F* centers. In fact, for temperatures
as low as 200°K the *F*-absorption band and the 1.43-eV
emission band actually overlap in their respective low-
and high-energy tails. On a naive single-configuration-
coordinate model this implies that the displacement of
the neighboring ions in lattice relaxation is small enough
to be comparable to their displacement in thermal
vibrations. The fact that the emission band is only 0.1
eV wide also suggests that the interactions of the
relaxed states with lattice vibrations are relatively weak
compared to those of most *F* centers, whose emission
bands are ~ 0.2–0.3 eV in width.

Another point is the short luminescent lifetime of
≈ 50 nsec, some ten times shorter than is generally
observed for *F* centers. Making the standard correc-

[10] W. B. Fowler, Phys. Rev. **135**, A1725 (1964).
[11] G. Spinolo and F. C. Brown, Phys. Rev. **135**, A450 (1964).
[12] R. Hetrick and W. D. Compton, Phys. Rev. **155**, 649 (1967).

tions for the index of refraction (1.47 for CsF) and the cube of the emission frequency (1.43 eV), this translates to an oscillator strength of ≈ 0.08, some ten times larger than that of the archetypical KCl F center, suggesting that the relaxed excited state of CsF is not diffuse compared to the relaxed ground state.

A third point is the thermal-activation energy of 0.19 eV, somewhat larger than that known for any other alkali-halide F center. According to the diffuse state picture this energy (or at least the energy required to make an optical transition to the conduction band, which is an upper bound on the thermal-activation energy) is given by a hydrogenic model and should scale inversely with the square of the effective dielectric constant. Spinolo[13] has determined the activation energies ΔE for F centers in several alkali halides and plotted them versus the square of ϵ_0, the *static* dielectric constant, demonstrating that this behavior is roughly obeyed, and at least ΔE decreases rapidly with increasing ϵ_0. The value of $\epsilon_0 = 7.90$ for CsF,[14] however, is larger than that of CsBr, 6.51, which would imply that ΔE for CsF should be less than ΔE for CsBr (0.04 eV) rather than 0.19 eV. These features all suggest that if the luminescence is a proper $P \rightarrow S$ transition, then the usual picture of diffuse relaxed excited states is not correct here.

Further support for this point of view can be gained from the optical-absorption properties. In Ref. 1 it was shown that the electron-lattice interactions which broaden the F-absorption band are primarily of non-cubic (Γ_{3g} and Γ_{5g}) symmetry. The interactions with cubic (Γ_{1g}) modes were found to be relatively weak, contributing only about one-fifth of the total second moment of the F band. As the lattice relaxation which produces the diffuse relaxed excited state in other F centers is cubic, this suggests again that the relaxed excited states in CsF are not diffuse.

Suppose as an extreme case that the properties of the P- and S-like electronic states are unaffected by the lattice relaxation. One can then make some comments based on the properties of the unrelaxed states as measured in Ref. 1. As described there, the effect of the cubic-mode interactions on the optical properties can be computed separately from those of the non-cubic modes, by alternately setting each interaction to zero and computing the line shapes, then convolving the two to yield the actual line shape. When the non-cubic mode interactions are set to zero the cubic-mode-only problem is just like the familiar problem of singlet-singlet transitions with linear electron-lattice coupling which predicts, among other things, mirror-image absorption and emission-band line shapes. If the interaction is taken simply as being with a single vibrational mode of effective energy ω_{eff}, the Stokes shift Γ_1 and the second moment of the absorption band

$\langle E^2 \rangle_1$ are related by $2\langle E^2 \rangle_1 = \hbar\omega_{eff}\Gamma_1$. For CsF a reasonable choice for $\hbar\omega_{eff}$ might be 75 cm^{-1}, and the value deduced in Ref. 1 of $\langle E^2 \rangle_1$ is $(37\,000 \pm 27\,000)$ cm^{-2} so that 1000 cm^{-1} ≈ 0.12 eV might be an approximate estimate of the Stokes shift due to the cubic modes only. In contrast, the Stokes shift in KCl is 1.1 eV, all consumed presumably in cubic lattice relaxation.

The noncubic-mode contributions to the electron-lattice interaction in the CsF F center are substantially larger than those of the cubic modes, although it is difficult to be quantitative about their contribution to the Stokes shift. Roughly, however, we might expect that the noncubic modes would cause $\approx 80\%$ of the Stokes shift, the same percentage they contribute to the F-band second moment. The lattice relaxation for noncubic modes would amount of course to a Jahn-Teller effect, which could be static in nature. Such a static Jahn-Teller distortion of, e.g., tetragonal (Γ_{3g}) symmetry would have the effect of suppressing trigonal (Γ_{5g}) contributions to the electron-lattice broadening of the emission band, and vice versa. Such an effect could help to explain why the second moment of the 1.43-eV emission band is 110 000 cm^{-2}, substantially smaller than the F-absorption-band second moment of 195 000 cm^{-2}. Ordinarily in F centers the emission band is broader than the absorption band.

The evidence from the optical absorption, then, suggests that the cubic lattice relaxation for the F center in CsF is not so large as in other alkali halides, and that the relaxed excited states might be affected by a Jahn-Teller distortion. This is consistent with the luminescence properties and further supports the suggestion that the relaxed excited states are not of the usually assumed diffuse variety.

In this scheme the observed dependence of the lattice-relaxation processes on whether the electron is excited to the $P_{1/2}$ or $P_{3/2}$ state could occur as follows. The charge distribution of the $P_{1/2}$ state has cubic (Γ_{1g}) symmetry and the $P_{1/2}$ state lies higher in energy than the $P_{3/2}$ state. Consequently the lattice relaxation will be purely cubic if the electron is excited to and remains in the $P_{1/2}$ state. A subsequent decay to the $P_{3/2}$ state would be followed by a noncubic (Jahn-Teller) distortion of the lattice. Excitation of the electron to the $P_{3/2}$ state directly would result immediately in both cubic and noncubic relaxation. The $P_{1/2}$ level of the two-level model would then correspond to the electron being in the cubically relaxed $P_{1/2}$ state. Note that the cubic relaxation in both the $P_{1/2}$ and the $P_{3/2}$ states would be the same, assuming the properties of the P-like states are not affected in the lattice relaxation.

B. Possible Origins of GSR Bottleneck

In deducing the existence of the metastable state from the GSR results we have assumed that the effect of the laser pulse is simply to transfer a substantial

[13] G. Spinolo, Phys. Rev. **137**, A1495 (1965).
[14] M. Hass, quoted as private communication in J. R. Hardy and A. M. Karo, Phys. Rev. **168**, 1054 (1968).

number of electrons into the relaxed excited state, after which they proceed as they would upon being excited by a less potent source. As pointed out by Mahr,[15] such an assumption fails if the laser wavelength also overlaps a second optical-absorption band arising from transitions from the usual excited state A to some higher level B. The laser pulse is sufficiently intense that in such a situation many of the centers could be "double pumped" into the higher level B. The GSR time would then reflect the recovery time for $B \rightarrow$ ground state, while the fast luminescence induced by the laser pulse could be just the luminescence from those centers which are only singly pumped, into A. In this situation, of course, the hypothesis of a metastable relaxed ground state is not required. Such a possibility cannot be completely ruled out without further experiments. Nevertheless, since at high temperatures the GSR time approaches the luminescent lifetime of 50 nsec, it would seem that any $B \rightarrow$ ground-state transition would proceed via level A and therefore result in a contribution to the 1.43-eV emission. At 10°K, then, this emission should show a 1-μsec decay time from the doubly pumped centers, which it does not. On this basis, it seems unlikely that the double pumping is occurring, and in what follows we shall continue to assume that the bottleneck is in the return to the unrelaxed ground state after the luminescence.

Possible explanations of the bottleneck are of two types. Either the effect is a true facet of the behavior of the isolated F center in a perfect CsF host lattice, or it is a dirt effect. In view of the difficulty of explaining a bottleneck in the lattice relaxation from relaxed to the unrelaxed ground state in the usual F-center picture, and in view of the unusual features of the alleged F-center luminescence, we discuss the latter possibility first.

Suppose that associated with most of the F centers is a neighboring impurity or trap of some sort. The following sequence of events can be visualized. The F-center electron is optically excited, the lattice relaxes, and somewhere in the process of lattice relaxation the electron is transferred to an excited state of the trap. The electron then decays to the ground state of the trap giving rise to the 1.43-eV emission. The ground-state wave function of the electron is then localized in the potential well which constitutes the trap, but the nearby charged vacancy encourages the return of the electron over or through the potential barrier between the vacancy and the trap by tunneling at low temperatures and also by Schottky emission at higher temperatures.

This picture explains in a natural, if not very interesting, way the lifetime discrepancy. The activation energy of 0.19 eV for photoconductivity and the luminescent properties in this case would be characteristic

of the trap rather than the F center and their unusual properties would be more understandable. Moreover, in view of the extreme deliquescence of CsF, the sample-dependent coloring difficulties described in Ref. 1, and the occasional cloudy appearance of the samples it is easy to believe that the samples are of low purity.

There are, however, important objections to the trap hypothesis: (a) These assumed traps are rather deep electron traps (emission energy of 1.43 eV) presumably present in concentrations at least as high as 2×10^{16} cm^{-3}, corresponding to the F-center concentration in the GSR experiments. The emission-band oscillator strength of 0.1 and the relatively narrow width of 0.1 eV suggest that one might find a correspondingly strong band in absorption. No absorption bands in this region of strength remotely approaching that of the F band are observed, even though a very brief x raying should be adequate to populate such traps. (b) The tunneling rate for the return of the electrons to the F-center ground state would ordinarily be expected to depend strongly on the distance between the trap and the F center. This makes it difficult to understand why the same decay rate of 1 μsec is observed both in the samples x rayed at liquid-nitrogen temperature and electrolytically colored at ≈ 500°C. Also note in Fig. 12 that the GSR recovery with time is approximately exponential for the decay of perhaps 80% of the excited centers. These features would require that the F centers are formed preferentially at fixed distances from such traps in both coloring processes. (c) Generally it might be expected that the luminescent behavior would be sample dependent or susceptible to changes by bleaching processes. Although such effects were not searched for diligently no obvious changes were observed in the luminescence properties for many different samples colored to concentrations ranging from 10^{15} to 2×10^{16} cm^{-3}, and in several cases thermally or optically bleached during the course of a run. (d) Essentially the same objections apply to assuming that the trap is not present in the crystal before coloring but is another species formed in the coloring process. An additional difficulty is that such a defect would have to be formed equally well by both coloring processes. (e) If the situation is one of transfer, it represents one of the most efficient energy-transfer processes between two isolated species known. For all these reasons it is difficult to accept the trap hypothesis as a solution to the GSR bottleneck problem.

We next assume the alternative possibility that the GSR bottleneck is an intrinsic property of the F center in CsF. It seems impossible that the metastable state could have a lifetime as long as 10^{-6} sec if it conforms to the usual F-center picture of the relaxed ground state differing only in a vibrational excitation of the surrounding ions. It is more likely that the explanation would lie outside this picture and involve processes not ordinarily associated with F centers. In what follows

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[15] H. Mahr, in *Physics of Color Centers*, edited by W. Beall Fowler (Academic, New York, 1968).

we speculate on various possible ways of accounting for the metastable behavior, although the experiments thus far do not select any particular model.

The schemes which one might conceive seem generally to involve either the assumption of additional electronic states of the F center or of some form of motion and displacement of the neighboring lattice ions. Fowler[16] has proposed an explanation which we use as an example of the first class. The usual S-like ground state of the CsF F center may be thought of roughly as composed of a symmetric linear combination of the $6s$ states of the six neighboring Cs^+ ions. Fowler points out that in the Cs^+ ion the $5d$ levels may lie sufficiently close in energy to the $6s$ that localized states of the F center derived from these $5d$ states might have energies comparable to those of the more usual S- and P-like states. He suggests that if the F-center electron were transferred into these states in the decay process then the return to the ground state could be bottle-necked. Assuming a particular level ordering in the relaxed lattice configuration he is also able to account for the temperature dependence of the bottlenecking.

The possibility of lattice ion motion as a source of metastability involves such events as displacement of one of the neighboring ions into an interstitial position in the lattice relaxation process. Such a strained configuration is classically stable, and would anneal at low temperatures by a tunneling process and higher temperatures by thermally assisted processes. Models of this sort are in part prompted by the large ratio of alkali-to-halide ionic radii of 1.86 Å to 1.16 Å,[17] which suggests the possibility of motion to the F^- ions provided there is sufficient strain in the lattice caused by the F-center excitation and possible Jahn-Teller lattice relaxation for the F center in its excited state. An example of a related color center in which ionic rearrangement is known to occur in the optically excited center is the type-II F_A center discussed by Lüty,[18] which is an F center having one of the nearest-neighbor alkali ions replaced by a foreign alkali ion of smaller ionic radius. In that case, however, the situation is

much more favorable as a result of the presence of the smaller ion, e.g., Li^+ in a KCl host lattice. An argument against such processes for the CsF F center is that less than 0.5 eV is consumed in the lattice relaxation, which seems a small energy to induce much ionic displacement. In contrast, in the type-II F_A centers anywhere from 1.2 to 1.5 eV of the absorbed 1.8- to 2.1-eV photon is consumed in the lattice relaxation.

VI. CONCLUSION

It is clear that further investigation of the optically excited F center in CsF will be necessary before a proper understanding of the curious behavior reported here can be achieved. For example, to investigate further the lattice relaxation it might be useful to extend the photoconductivity and Schottky ionization measurements, respectively, to lower and higher temperatures. A study of the effect of uniaxial stress on the 1.43-eV emission could prove more fruitful than in other F centers because the postulated compact excited state would presumably be more strain sensitive than the standard diffuse states. To study further the metastable behavior it could be useful to repeat the Fröhlich-Mahr experiment looking for transient absorptions due to the momentary population of the intermediate decay levels, both the relaxed excited state and the metastable level. These could be expected to show characteristic time behavior. For instance, absorptions from the metastable level should show a 50-nsec rise time and 1-μsec decay time at low temperatures.

From the studies reported here, it appears that the eventual understanding of the behavior of this center will require revision of the current models of the decay modes of the excited F center. Both this work and the optical-absorption properties reported in Ref. 1 indicate that the F center in CsF should be included as an important test case in future studies of the properties of F centers in the alkali halides.

ACKNOWLEDGMENTS

[16] W. B. Fowler, Phys. Rev. **174**, 988 (1968).
[17] B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1960), Vol. 10.
[18] F. Lüty, in *Physics of Color Centers*, edited by W. Beall Fowler (Academic, New York, 1968).