

when the surface scattering is effective for grazing angles, but not when grazing electrons are specularly reflected. This explains the absence of a cusp for the InSb surfaces studied by Davis,<sup>3</sup> provided we infer that these surfaces have scattering mechanisms which are ineffective for grazing electrons. Such an inference, although necessarily provisional in the absence of a treatment of the energy dependence of  $\rho$ , is interesting, inas-

much, as it agrees with the conclusion reached by Aubrey *et al.*<sup>5</sup> and Parrott<sup>6</sup> for the semimetal Bi at 4.2°K.

#### ACKNOWLEDGMENT

It is a pleasure to thank John Davis for a critical reading of the manuscript and for several valuable suggestions.

### Decay of Laser-Induced Excitations of $F$ Centers\*

DIETMAR FRÖHLICH AND HERBERT MAHR

*Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York*

(Received 9 August 1965)

A strong population of excited  $F$ -center states is achieved in various alkali halides using a short intense pulse of a  $Q$ -switched ruby laser. During the presence of the excited  $F$  centers the time dependence of their decay is measured with a fast-recording spectrometer. This is done by monitoring the absorption changes connected with the ground-state or excited-state populations. Using this method for crystals containing low  $F$ -center concentrations, the lifetime of the excited state of  $F$  centers in KI, RbI, CsI, RbBr, and CsF is measured from 7 to about 80°K by monitoring absorption changes in the region of the  $\beta$ , the  $\beta^*$  and the  $F$  band, respectively. For KI samples containing high  $F$ -center concentrations it is found that the decay curves are nonexponential.

#### I. INTRODUCTION

THE knowledge of the lifetime of excited states is important for the understanding of the character of electronic transitions in solids. Allowed electric dipole transitions are expected to have lifetimes of the order of  $10^{-8}$  sec. Recently, however, Swank and Brown<sup>1</sup> found for the excited state of  $F$  centers in some alkali halides lifetimes of the order of  $10^{-6}$  sec. These results were rather surprising in view of the high absorption cross section of the  $F$  transition, and they stimulated a variety of theoretical considerations<sup>2</sup> on the nature of this excited state. A number of alkali halides have since been studied<sup>3</sup> by conventional techniques: After flash excitation of the  $F$  center by a very short light pulse the resultant decay of luminescence or photoconductivity was determined. Photoconductivity measurements were limited, however, to a temperature region where a sufficient concentration of electrons is still thermally stimulated into the conduction band from

the excited state  $F^*$  of the  $F$  center. The lowest temperatures reached were about 70°K ( $F$  centers in KI, KBr, RbBr, and CsBr).<sup>1,3</sup> Luminescence measurements, on the other hand, were limited by the availability of fast detectors in the infrared region to  $F$  centers in KCl, NaCl, and RbCl.<sup>1,3</sup>

This paper reports measurements of the radiative lifetime of  $F$  centers in several alkali halides extending the range of observations to lower temperatures (in KI and RbBr) and other crystals (RbI, CsI, and CsF). The method is novel in that it employs a very intense, short light pulse from a  $Q$ -switched ruby laser, which in contrast to conventional methods pumps an appreciable number of the  $F$  centers in the specimen into the excited state. These changes of population of the ground state and the excited state are so large that transmission changes of the sample can now be directly observed with a fast-recording spectrometer. Because these changes occur in *any* of the various absorption bands connected with the ground or excited state of the  $F$  center, the time dependence of these population changes can be studied in various regions of the visible and near uv. The monitoring light source of the spectrometer, a xenon flash lamp, can be made sufficiently intense so that a rather good signal-to-noise ratio is achieved. In addition changes of population of the ground state and the excited state can be monitored independently. The method could therefore be used to check upon the exponential nature of the decay of population changes. For higher  $F$  concentrations in KI nonexponential decay curves were indeed observed.

\* Work supported by the U. S. Office of Naval Research and the Advanced Research Projects Agency.

<sup>1</sup> Robert K. Swank and Frederick C. Brown, *Phys. Rev. Letters* **8**, 10 (1962); *Phys. Rev.* **130**, 34 (1963).

<sup>2</sup> W. Beall Fowler and D. L. Dexter, *Phys. Rev.* **128**, 2154 (1963); S. I. Pekar and Yui E. Perlin, *Zh. Eksperim. i Teor. Fiz.* **43**, 1108 (1962) [English transl: *Soviet Phys.—JETP* **16**, 782 (1962)]; W. Beall Fowler and D. L. Dexter, *Phys. Status Solidi* **3**, 1865 (1963); W. Beall Fowler, *Phys. Rev.* **135**, A1725 (1964).

<sup>3</sup> Giorgio Spinolo and Frederick C. Brown, *Phys. Rev.* **135**, A450 (1964); G. Gramm, *Phys. Letters* **8**, 157 (1964); Giorgio Spinolo, *Phys. Rev.* **137**, A1495 (1965).

## II. EXPERIMENTAL METHOD

The experimental method utilizes a megawatt ruby laser source of approximately 30-nsec duration to achieve a strong population of excited states. The changes of population of ground and excited states are measured independently by monitoring the absorption connected with the ground or excited states.

A schematic diagram of the experimental setup is shown in Fig. 1. The transmitted light intensity  $I = I_0 \exp(-k_0 d)$  from a millisecond flash of a xenon arc is monitored by a photomultiplier and displayed on oscilloscope 1 with a slow sweep speed of 2 cm/msec. Changes  $\Delta I(t)$  of transmission induced by the 30-nsec laser pulse are monitored by the same photomultiplier and are displayed by means of a high pass filter on oscilloscope 2 with a fast-sweep speed of about 1 cm/ $\mu$ sec.

For the  $F$  center in suitable alkali halides, absorption of the ruby-laser light leads to the excitation of  $N^*(0)F$  centers to a state which decays very fast ( $< 10^{-10}$  sec) by emission of phonons to the so-called relaxed excited state  $F^*$ . Typically the laser pulse delivered 5 MW (corresponding to  $5 \times 10^{17}$  photons per pulse) and pumped in excess of 90% of the  $F$  centers to the excited state. With the monochromator set to any absorption band of the  $F$ -center ground state ( $F$ ,  $K$ ,  $L$ , or  $\beta$  bands) an increase in transmission is observed, indicative of a depopulation of the ground state. With the monochromator set to any absorption band of the relaxed excited state ( $F^*$ -absorption band<sup>4</sup> or  $\beta^*$  band<sup>5</sup>) a decrease in transmission is observed indicative of a population of the excited state. The time dependence of these measured changes in transmission  $\Delta I(t)$  are simply connected to changes in the population of the ground state  $\Delta N(t)$  and the excited state  $\Delta N^*(t)$ .

The increase in transmission  $\Delta I(t)$  ( $F$ ,  $K$ ,  $L$ , and  $\beta$  bands) is given by

$$\Delta I(t) = I_0 \exp\{-(k_0 - \Delta k(t))d\} - I_0 \exp\{-k_0 d\}, \quad (1)$$

where  $k_0$  is the absorption constant of  $N_0 F$  centers in the ground state ( $k_0 = \gamma N_0$ ) and  $\Delta k(t)$  is the change of absorption constant caused by the reduction of the number of centers in the ground state. With  $\Delta k(t) = \gamma \Delta N(t)$  and defining  $A(t) = \Delta I(t)/\Delta I(0)$  we get from (1)

$$\Delta N(t)/\Delta N(0) = [\Delta k(0)d]^{-1} \times \ln\{A(t)[\exp(\Delta k(0)d) - 1] + 1\}. \quad (2)$$

The normalized change of the ground-state population  $\Delta N(t)/\Delta N(0)$  can thus be calculated directly from measured quantities:  $A(t)$  can be taken from the trace of oscilloscope 2 and  $[\exp(\Delta k(0)d) - 1]$  can be easily

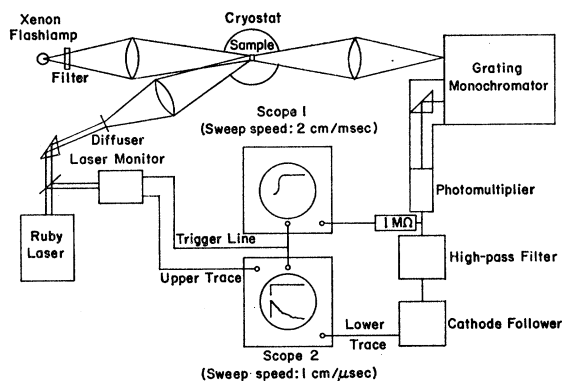


FIG. 1. Schematic diagram of the experiment.

deduced from the measured signals on oscilloscope 1 and 2 through

$$[\exp(\Delta k(0)d) - 1] = \Delta I(0)/I_0 \exp(-k_0 d). \quad (3)$$

The decrease in transmission  $\Delta I(t)$  ( $F^*$  and  $\beta^*$  band) due to the population  $N^*(t)$  of the excited state is given by

$$\Delta I(t) = I_0 - I_0 \exp\{-\Delta k^*(t)d\}, \quad (4)$$

if for simplicity we measure in a spectral region where no absorption due to  $F$  centers in the ground state is observed. With  $\Delta k^*(t) = \gamma^* \Delta N^*(t)$  we get from Eq. (4)

$$\Delta N^*(t)/\Delta N^*(0) = -[\Delta k^*(0)d]^{-1} \ln\{1 - \Delta I(t)/I_0\}. \quad (5)$$

The normalized decay of the excited state population  $\Delta N^*(t)/\Delta N^*(0)$  can thus be obtained directly from the measured quantities  $\Delta I(t)$  and  $I_0$ .

The sample was mounted in a conduction helium cryostat; the samples could be cooled to a lowest temperature of about 7°K. The single crystals used were purchased from the Harshaw Chemical Company (KI, CsI, and CsF) and Semi Elements, Inc. (RbBr). The RbI crystals were grown from UHP grade powder (Merck, Germany) in the Crystal Growth Facility of the Materials Science Center of Cornell University. The  $F$  centers were formed by additive coloration (CsI and KI) as well as electrolytic coloration (KI, RbBr, RbI, and CsF). Before mounting, the crystals were heated above 350°C and quenched in the dark. The cryostat which was used allowed routine optical measurements of the sample in a Cary Model 14 spectrophotometer in between the lifetime measurements to check the  $F$ - and  $F'$ -center concentration of the crystals after the intense illumination by the red ruby light.

## III. RESULTS

Figure 2 shows typical oscilloscope traces obtained with samples containing less than  $5 \times 10^{16}$  ( $F$  centers)/cc at 7°K. For the traces on the left-hand side the spectrometer was set to an absorption band connected with the excited state ( $\beta^*$  band<sup>5</sup>). The upper trace records the transmission through the spectrometer during the

<sup>4</sup> Kwangjai Park, thesis, University of California, Berkeley, 1965 (unpublished), and Phys. Rev. (to be published).

<sup>5</sup> Dietmar Fröhlich and Herbert Mahr, Phys. Rev. Letters 14, 494 (1965).

duration of the xenon flash as seen on oscilloscope 1 (transmission is recorded downward by the photomultiplier). At the time the laser is pulsed the transmission drops suddenly by an appreciable part due to the population of the excited state. The transmission through the sample recovers then with the characteristic lifetime of the excited state. This part of the curve is enlarged in the lower photo (as seen on oscilloscope 2). For the traces on the right-hand side, the spectrometer was set to an absorption connected with the  $F$  ground state ( $F$  band in this case). The upper trace shows again the transmitted light intensity (decreased now due to absorption by  $F$  centers) during the duration of the xenon flash. At the time the laser is pulsed the transmission increases appreciably due to the complete depopulation of the  $F$  ground state. This part of the curve is enlarged below showing the repopulation of the  $F$  ground state.

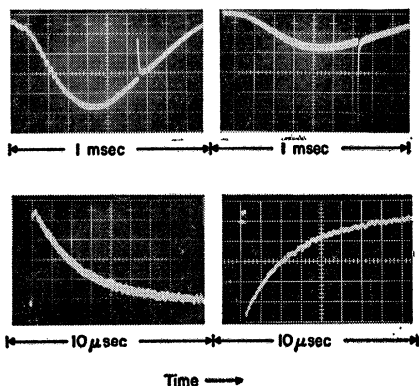


FIG. 2. Typical oscilloscope traces. Left: Induced transmission decrease due to a change of the excited-state population as seen on oscilloscopes 1 and 2. Right: Induced transmission increase due to a change of the ground-state population as seen on oscilloscope 1 and 2. (Transmission is recorded downward by the photomultiplier).

For a thick crystal containing  $2 \times 10^{16}$  ( $F$  centers)/cc the relative transmission change was taken from oscilloscope traces similar to the ones of Fig. 2 and plotted semilogarithmically in Fig. 3. Curve (a) gives the result of the normalized increase in transmission  $A(t)$  in the maximum of the  $F$  band ( $660 \text{ m}\mu$ ), whereas curve (b) shows the data points for the normalized decrease of transmission in the  $\beta^*$  band ( $240 \text{ m}\mu$ ). For such a thick crystal the two transmission decay curves, as observed, look very different. However, using formulas (2) and (5) to calculate the population changes  $\Delta N(t)/\Delta N(0)$  and  $\Delta N^*(t)/\Delta N^*(0)$  we find [curve (c)] that both populations decay exponentially with the same lifetime  $\tau$  as expected. The accuracy of such plots is certainly good enough to establish the exponential character of the decay. In this manner the lifetime of the excited state of the  $F$  center in KI was determined as a function of temperature (Fig. 4) for samples containing low  $F$ -center concentrations. The results were

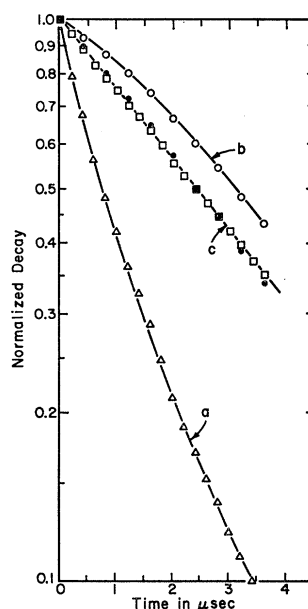


FIG. 3. Semilogarithmic plot of the normalized transmission increase [curve (a)] due to a change of the ground-state population and the normalized transmission decrease [curve (b)] due to a change in the excited-state population. Curve (c) is the calculated normalized change of the ground- and excited-state populations respectively [ $\square$  calculated from curve (a);  $\bullet$  calculated from curve (b)].

obtained using very different wavelength regions, at  $227 \text{ m}\mu$  ( $\beta$  band), at  $240 \text{ m}\mu$  ( $\beta^*$  band) and  $660 \text{ m}\mu$  ( $F$  band). For comparison data of Swank and Brown<sup>1</sup> are added. Their values of  $\tau$  were obtained from photoconductivity pulses.

The same method was used to determine the lifetime of excited  $F$  centers of RbI, CsI, and RbBr by measuring the decrease of transmission in the  $\beta^*$  band and for CsF by measuring the increase of transmission in the  $F$  band. All these measurements were done with low  $F$ -concentration samples. The results are plotted in Fig. 5.

For the highest temperature points of each crystal of Fig. 5 the decay curve was still exponential at the beginning but decayed noticeably slower for longer decay times. The effect becomes more pronounced as the temperature rises. The lifetime was determined from the initial slope in these cases.

KI samples containing more than  $5 \times 10^{16}$  ( $F$  centers)/cc showed decay curves which were clearly nonexponen-

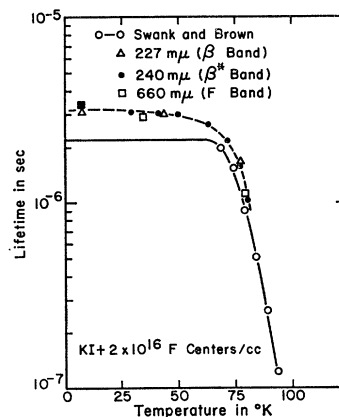
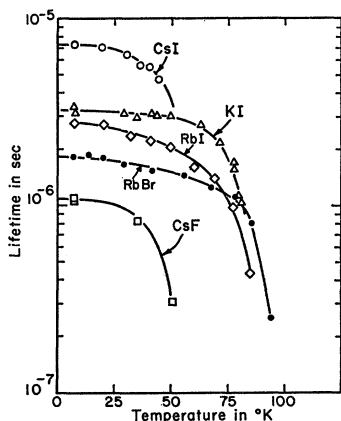


FIG. 4. Lifetime  $\tau$  of the excited state of  $F$  centers in KI versus temperature. Data points were calculated from transmission changes in the region of the  $\beta$ -,  $\beta^*$ - and  $F$ -band absorption. For comparison lifetime data of Swank and Brown obtained from photoconductivity pulses are added.

FIG. 5. Lifetime  $\tau$  of excited *F* centers in CsI, RbI, KI, RbBr, and CsF versus temperature.



tial at 7°K. With increasing *F*-center concentration the initial decay of the excited-state population gets faster. Detailed measurements of this and related phenomena are under way and will be reported separately.

#### IV. DISCUSSION

Several possible causes of the long lifetime of the *F*-excited state *F*\* have been discussed by Swank and Brown.<sup>1</sup> Fowler<sup>2</sup> has recently worked out in detail a suggestion that the relaxed excited state of the *F* center is very diffuse. He got quantitative agreement with experiments on Stokes' shift and lifetime for NaCl. Spinolo,<sup>3</sup> taking up Fowler's suggestion of a very diffuse excited state, approximated the wave function of the state by a hydrogenic  $n=2$  function. He got reasonable agreement of the measured thermal activation energies from the excited state to the conduction band of various alkali halides. A quantitative formulation of the variation of the lifetime of various alkali halides with parameters of these salts has not been given yet. We find experimentally that the iodides have the longest lifetime and that among the metal ions the Cs salts have the largest values of  $\tau$ . It should be cautioned here that in all cases the lifetime increases still in the temperature region between 60°K and He temperature as observed by Swank and Brown<sup>1</sup> for KCl. This slow rise makes the comparison of lifetime data measured at He temperatures with those extrapolated from higher temperatures to He temperature difficult.

As pointed out by Swank and Brown<sup>1</sup> the lifetime decreases at higher temperatures because of the possibility of thermal activation out of the excited state into the conduction band. With conventional ways of measuring the lifetime by using spark gaps for excita-

tion, the concentration of excited states is only a small fraction of the total concentration of centers. Following activation to the conduction band, very few electrons will therefore return during the observation time to an excited state by recombination. The decay curve remains exponential although the lifetime is changed to  $1/\tau' = 1/\tau + \nu_0 \exp(-\Delta E/kT)$ . However, the strong population of the excited state achieved with the laser source changes the simple picture. The loss of population through radiative decay (with probability  $P_r = 1/\tau$ ) and thermal activation [ $P_{th} = \nu_0 \exp(-\Delta E/kT)$ ] will be reduced by a gain of excited states *F*\* through recombination of conduction-band electrons with vacancies. Because the concentration of conduction-band electrons is small initially (at modest temperatures) and will build up as time progresses, the recombination effect will not alter the decay curves initially. As observed experimentally, however, there is a noticeable slowdown of the decay at later times.

As long as the sample is sufficiently diluted so that neighboring centers do not interact with each other, *F* centers can only decay by radiation at 7°K. For strong population of excited *F* centers this is no longer true for samples containing more than  $5 \times 10^{16}$  (*F* centers)/cc in KI. Park<sup>4</sup> recently discovered that absorption from the relaxed excited state overlaps the emission band of this same state. Excited centers can therefore decay by transfer in addition to radiative decay.<sup>6</sup> This transfer can be accomplished via dipole-dipole interaction, exchange interaction, or through self-absorption of emitted light. All these interactions will give rise to nonexponential decay curves because the transfer probability depends on the concentration of excited states in each case. A detailed comparison of experimental decay curves with predictions of these various transfer mechanism will be reported separately.

#### ACKNOWLEDGMENTS

The authors would like to thank Professor R. O. Pohl and D. A. Bower and J. Francis of the Crystal Growth Facility of the Materials Science Center for the growth of high-purity RbI crystals. The help of T. A. Fulton in handling the CsF samples is much appreciated.

<sup>6</sup> Th. Förster, Z. Elektrochem. **53**, 93 (1949); Angew. Chem. **59**, 181 (1947); **60**, 163 (1948); Z. Naturforsch. **4a**, 321 (1949); D. L. Dexter, J. Chem. Phys. **21**, 836 (1953); D. L. Dexter and James H. Schulman, J. Chem. Phys. **22**, 1063 (1954); K. B. Eisenthal and S. Siegel, J. Chem. Phys. **41**, 652 (1964).

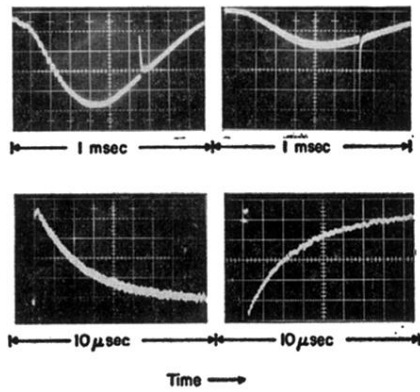


FIG. 2. Typical oscilloscope traces. Left: Induced transmission decrease due to a change of the excited-state population as seen on oscilloscopes 1 and 2. Right: Induced transmission increase due to a change of the ground-state population as seen on oscilloscope 1 and 2. (Transmission is recorded downward by the photomultiplier).