

Lifetime of the Excited F Center*

ROBERT K. SWANK† AND FREDERICK C. BROWN

Department of Physics, University of Illinois, Urbana, Illinois

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An investigation was carried out on the excited state of the F center in various alkali halide crystals as a function of temperature. Results are presented on the time dependence of photoconductivity and luminescence following excitation by a very short, 10^{-8} sec, pulse of light. The data can be interpreted in terms of a simple energy-level diagram of the F center consisting of a ground state and an excited state. Estimates are given of the depth of the excited state below the conduction band ΔE , the frequency factor for thermal ionization $1/\tau_0$, and the radiative lifetime τ_R , for KCl, KBr, KI, and NaCl. The radiative lifetime τ_R depends upon the alkali halide, but may be as long as 10^{-6} sec. Suggestions are made for understanding this long lifetime in view of the large oscillator strength of the F center. The effect of F -center concentration and also of an admixture of M centers is discussed.

I. INTRODUCTION

THE F center in an alkali halide crystal is known to be an electron trapped at a negative-ion vacancy. A simple energy-level diagram for the center would consist of a $1s$ ground state and a $2p$ excited state lying a few tenths of an electron volt below the bottom of the conduction band. The situation is complicated, however, by the fact that upon excitation the lattice relaxes around the center. The interaction between the electron and the ionic lattice is strong and furthermore cannot be treated in the continuum approximation, at least as far as the ground-state wave function is concerned.^{1,2} Nevertheless, recent experimental results³ on F centers excited by very short pulses of light show that the temperature dependence of the lifetime, the fluorescent yield and the photoconductivity can be interpreted in terms of the familiar two level model. This model leads to the following simple equations for the lifetime of the excited state τ , the fluorescence yield η_R , and the yield of free electrons η_i , to which photoconductivity is proportional:

$$\tau = \frac{\tau_R}{1 + (\tau_R/\tau_0)e^{-\Delta E/kT}}, \quad (1)$$

$$\eta_R = \frac{\tau}{\tau_R} = \frac{1}{1 + (\tau_R/\tau_0)e^{-\Delta E/kT}}, \quad (2)$$

$$\eta_i = \frac{\tau}{\tau_i} = \frac{1}{1 + (\tau_0/\tau_R)e^{\Delta E/kT}}. \quad (3)$$

The first of these equations follows by simply adding a temperature-dependent probability for thermal ionization $1/\tau_i = (1/\tau_0)e^{-\Delta E/kT}$ to the probability for radiative

recombination $1/\tau_R$. A temperature-dependent non-radiative recombination term is neglected. Also, re-trapping of free electrons in the empty F center is omitted since only a small fraction of the total number of centers are excited during a pulse and there is strong trapping by other F centers.

In the aforementioned experiments³ it was found that the excited-state lifetimes determined from the decay of photoconductivity and luminescence were identical. Moreover, the values of radiative lifetime τ_R were unexpectedly large, being of the order of 10^{-6} sec rather than 10^{-8} sec.⁴ More complete results are given in the present paper. These include the effect of F center concentration as well as the influence of M centers on the excited-state lifetime.

II. EXPERIMENTAL DETAILS

The F band was excited by a pulse of light having a width of $0.018 \mu\text{sec}$ at half-maximum. This light pulse was derived from a spark between stainless steel electrodes, separation 1 mm, in nitrogen gas at a pressure of about $\frac{2}{3}$ of an atm. A capacitor of $1000 \mu\mu\text{F}$ was discharged in an arrangement having an inductance as low as 5×10^{-9} H, operating as a relaxation oscillator from a supply potential of 5000 V. A narrow region of wavelength suitable for excitation of the F band was selected by means of filters from the broad spectrum emitted. In some cases, a range of shorter wavelengths was used for the purpose of exciting one or more of the L bands.⁵ This procedure was useful for purposes of comparison, since the L transitions lead to excited states which are not bound. Fluorescence was detected with a photomultiplier, type 7102, while the pulses of photoconductivity were amplified by a low-noise cascode preamp and wide band oscilloscope. Single transient waveforms were photographed, analyzed, and replotted on semi-logarithmic graph paper. Lifetimes were determined from the slopes of such plots, while the relative yields were obtained from the pulse heights, with suitable optical attenuators placed in the light beam.

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† National Science Foundation Predoctoral Fellow. Present address: General Electric Research Laboratory, Schenectady, New York.

¹ W. B. Fowler and D. L. Dexter, *Phys. Rev.* **128**, 2154 (1962); see also, *Phys. Stat. Sol.* **2**, 821 (1962).

² B. S. Gourary and A. E. Fein, *J. Appl. Phys.* **33**, 331 (1962).

³ R. K. Swank and F. C. Brown, *Phys. Rev. Letters* **8**, 10 (1962).

⁴ J. J. Markham, *Bull. Am. Phys. Soc.* **7**, 197 (1962).

⁵ F. Lüty, *Z. Physik* **160**, 1 (1960).

All the results reported here were obtained with crystals additively colored by heating in the appropriate alkali vapor. Samples cut from the colored crystals were placed in an oven for 30 to 60 sec and were then quenched from high temperature by placing on a copper block. The temperature before quenching was 600°C for KCl and NaCl, 400°C for KBr, and 350°C for KI. The samples were 0.5–1.0 mm thick and about 5 mm square. They were handled under red safelight conditions following coloration and quenching.

The various alkali halide crystals were purchased from the Harshaw Chemical Company. There was no detectable absorption, fluorescence, or photoconductivity in the uncolored crystals under *F*-band irradiation. Hence, impurities were present in sufficiently low concentration not to be the source of electrons. However, impurities played a role in the trapping of photoelectrons in lightly colored samples. It is well known^{6,7} that shallow electron traps can produce, in an appropriate temperature range, a "lifetime" for the photoconductivity that is essentially a measure of the time spent in traps. Such effects were observed in these crystals when the *F*-center concentration was of the order of $10^{15}/\text{cm}^3$. It was possible, however, to distinguish between these effects and the effect of interest here: the lifetime for release of the electron from the excited *F* center into the conduction band. At *F*-center concentrations above $10^{16}/\text{cm}^3$, shallow trapping was not significant. In this concentration range, the shallow traps were unimportant compared to the deep trapping of the *F* centers. Electron trapping at *F* centers leads to the formation of *F'* centers which are only stable for about 10^{-1} sec near room temperature. This time, however, is essentially infinite compared with the time of observation, 10^{-8} to 10^{-4} sec.

Even in the absence of shallow trapping, one might expect the time spent by the photoelectron in the conduction band would be a contributing factor to the measured photoconductive lifetime. This was never the case in these experiments. Even at low *F*-center concentrations, the lifetime of the free conduction electron was less than 10^{-8} sec. With *F*-center concentrations above $10^{16}/\text{cm}^3$, it should be less than 10^{-9} sec.

In the measurement of photoconductivity, it is necessary to apply an electric field to the crystal. Because of the short free lifetime of the conduction electrons, the distance of drift in the field was very small, usually 1/1000 of the crystal thickness. Under these conditions, the signal is proportional to the applied field. In the interest of a good signal-to-noise ratio, a high field is desirable. On the other hand, it is known that ionization of the excited *F* center is enhanced in a high field by the mechanism of the internal Schottky effect, operating in this case on the excited state.⁸ It was necessary to find a compromise between these two

conflicting factors. The electric fields used were in the range 2–7 kV/cm. In this range, the effects of internal Schottky emission were small, but measurable. A correction was applied when significant. The correction, which consisted of a shift in the temperature scale, was determined by varying the field at selected points, and extrapolating to zero field. The magnitudes of the corrections ranged from 1 to 5°K.

III. RESULTS

A. *F* Centers in KCl

The relative photoconductivity of a crystal of KCl containing 2×10^{16} *F* centers/cm³ is shown as a function of the temperature in Fig. 1. The curve for *F*-band irradiation follows the familiar form reported previously by several authors, particularly by the group at Göttingen.⁹ The rapid decrease in the photoconductivity with temperature in the region near 100°K has been established as the freezing-in of the excited state, in accordance with Eq. (3). However, the curve is somewhat distorted by the variation of the mobility with temperature. The curve shown for *L*-band irradiation has not been reported before. Since the excited state reached in the *L* transition lies above the bottom of the conduction band, the absorption band should be photoconducting at all temperatures, so that the curve shows only the change of mobility with temperature. However, a small, but well-defined dip occurs in this curve

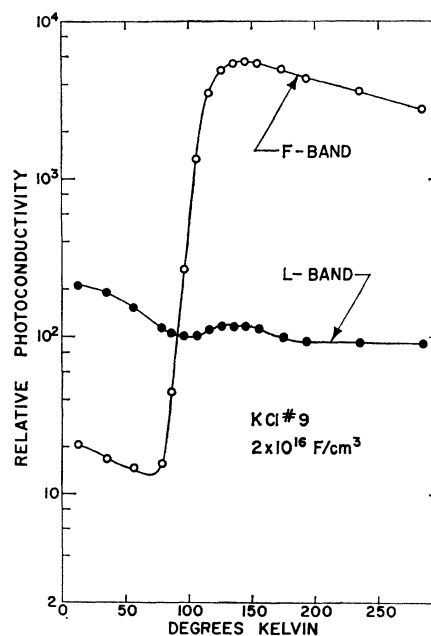


FIG. 1. Relative photoconductivity of KCl sample number 9, for irradiation in the *F* band (Corning filters CS-4-94 plus CS-3-71) and in the *L* bands (filter CS-7-54). No correction has been applied for the small effect of the electric field which was 3.3 kV/cm.

⁶ J. A. Hornbeck and J. R. Haynes, Phys. Rev. **97**, 311 (1955).

⁷ A. Rose, Phys. Rev. **97**, 322 (1955).

⁸ F. Lüty, Z. Physik **153**, 247 (1958).

⁹ H. Rögner, Nachr. Akad. Wiss. Göttingen Math. Physik Kl. Ila **3**, 219 (1941).

in about the same place as in the F -band curve. There are two possible explanations for this behavior: (1) The higher excited state reached in the L transition decays part of the time into the first excited state before autoionization occurs; (2) the dip is caused by trapping at α centers (empty F centers). Since such trapping is predominantly into the excited state, competition between thermal re-emission and decay to the ground state takes place in the same way as when an F center is raised into the first excited state by light. Thus, one expects an enhanced trapping at just the temperature where the photoconductivity of the F center declines.

The fact that the F -band photoconductivity does not continue to fall according to Eq. (3) at very low temperatures is well known. This low-temperature residue is most likely a photoconductivity arising from some other centers, such as F -center aggregates, or metal colloids.

Although the curve of photoconductivity vs temperature deviates from Eq. (3) because of the factors mentioned, the curve of relative fluorescence yield follows the theoretical expression given by Eq. (2) very well. This is seen in Fig. 2 for the same crystal. In this figure, the solid line is a plot of Eq. (2) with appropriately chosen parameters, while the points are measured values.

Equations (1) and (2) predict identical temperature dependence for the fluorescence yield and the lifetime of the excited state. The lifetimes for this specimen are given in Fig. 3. The lifetime values obtained from fluorescence pulses fall nicely on the same curve as those obtained from photoconductivity. The data

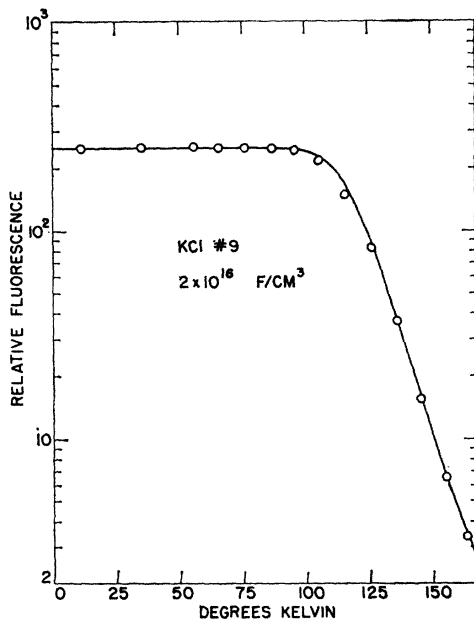


FIG. 2. Relative fluorescence of KCl sample number 9 for irradiation in the F band. The solid line is a plot of Eq. (2) with $\Delta E = 0.164$ eV and $\tau_R/\tau_0 = 7.5 \times 10^6$.

follow a curve that has the general form Eq. (1), but it is not possible to fit it exactly. The solid curve has been fitted to the data in the region of the rapid fall, at the expense of the low-temperature points. This gives parameters which are not greatly different from those obtained from the fluorescence yield. The tendency of the low-temperature points to rise above the solid curve will be discussed later in connection with the question of the long radiative lifetime. Data from photoconductivity are not available at low temperatures, because the yield becomes vanishingly small. The photoconductivity which does remain at low temperatures exhibits a decay constant which is at least an order of magnitude shorter than that of the F center.

Figure 4 shows the photoconductivity of a crystal with 15-fold higher concentration of F centers. Two differences are noted: First, the low-temperature residue of the F -band curve is greater than before. Since absorption measurements show that a measurable M band is present at this concentration, a relationship between these centers and the low-temperature residue is suggested. Second, the dip in the L -band curve near 100°K is reduced so that this curve follows the change in mobility more closely. If the dip is caused by trapping at α centers, then it should be reduced at higher F -center concentrations because of the increased competition by deep trapping at F centers.

The dependence of the fluorescence yield on the temperature was essentially the same as shown for the previous sample in Fig. 2. One difference was a small

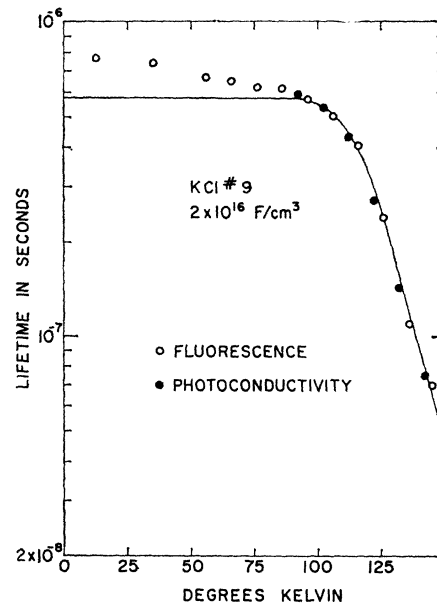


FIG. 3. Lifetimes of fluorescence and photoconductivity of KCl sample number 9, determined from the shape of the same pulses whose pulse heights are given in Figs. 1 and 2. A shift of 5°K has been made in the photoconductivity points to compensate for the field of 3.3 kV/cm. The solid line is a plot of Eq. (1) with $\Delta E = 0.142$ eV, $\tau_R = 0.578$ μsec , and $1/\tau_0 = 1.2 \times 10^{12}$ sec^{-1} .

amount of fluorescence at high temperatures, arising from M centers. This fluorescence was excited by irradiation in the F band.

In order to illustrate the dependence of the lifetime on F -center concentration, curves of the fluorescence lifetimes vs temperature are shown in Fig. 5 for three different concentrations. There appears to be no significant difference in the lifetime between the samples with 2×10^{15} and 2×10^{16} F centers/cm³, but the lifetime at low temperatures is smaller by about 20% for the sample with 3×10^{17} F centers/cm³.

B. Other Materials

In addition to KCl, investigations were made of the F centers in KBr, KI, and NaCl. Since the results are very similar to those for KCl, only a few interesting examples are shown here. The photoconductivity of a sample of KBr with 4×10^{16} F centers/cm³ is shown in Fig. 6. The loss of photoconductivity takes place at a lower temperature than for KCl. (For KI, the temperature is still lower.) One interesting feature of this curve is the complete absence of the dip in the L -band curve. Another sample of KBr, with a smaller concentration of F centers, showed the usual dip, as did all samples of KCl, KI, and NaCl. This clearly shows that the dip is a structure-sensitive phenomenon.

Figure 7 shows the photoconductive lifetimes for two crystals of KBr with different concentrations of F centers. No fluorescence measurements were made on KBr or KI, because the wavelengths of emission were beyond the long-wavelength limit of the photomultiplier.

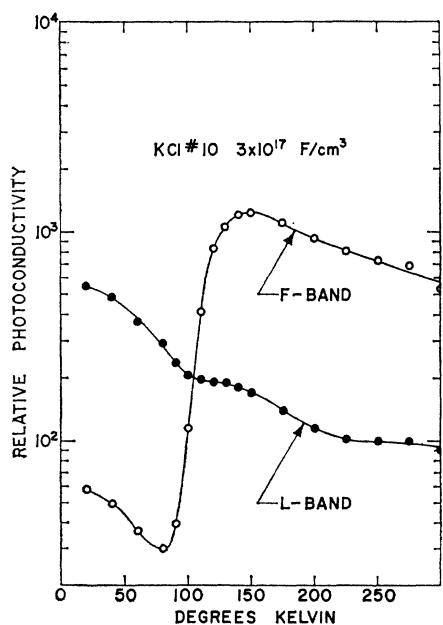


FIG. 4. Relative photoconductivity of KCl sample number 10, for irradiation in the F band, and the L bands. No correction has been made for the applied field, which was 6.9 kV/cm.

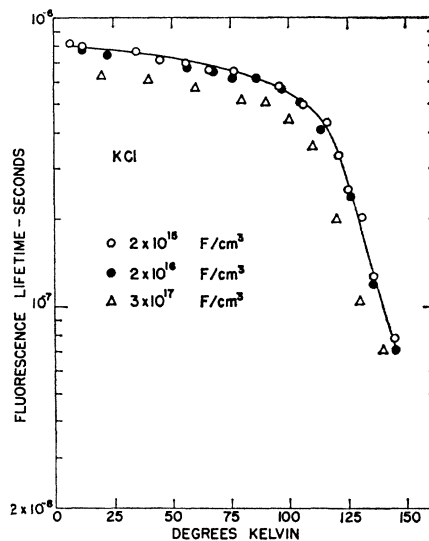


FIG. 5. Lifetime of fluorescence of KCl samples number 8, 9, and 10, plotted together to show the effect of concentration.

Table I summarizes the results obtained by fitting Eqs. (1) and (2) to the data obtained from a number of crystals. The last column of the table gives the value of the capture cross section of the α center, using the relation between the escape-frequency factor $1/\tau_0$ and the capture cross section σ obtained for a simple trapping level by the method of detailed balancing:

$$\sigma = 3.3 \times 10^{-22} g(m/m^*) (1/T^2) (1/\tau_0), \quad (4)$$

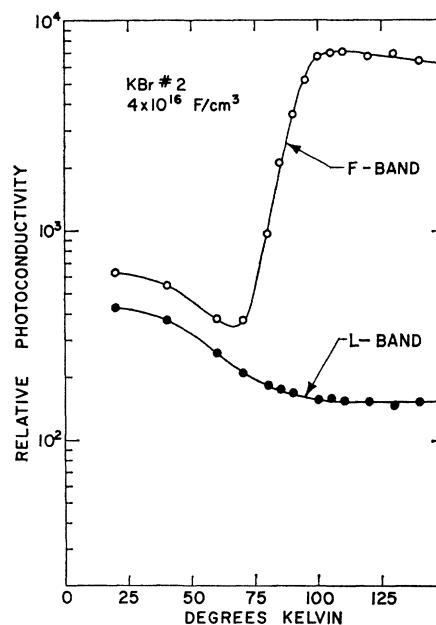


FIG. 6. Relative photoconductivity of KBr sample number 2, for irradiation in the F band (Corning filter CS-3-68) and the L bands (filter CS-7-54). No correction has been applied for the electric field of 3.8 kV/cm.

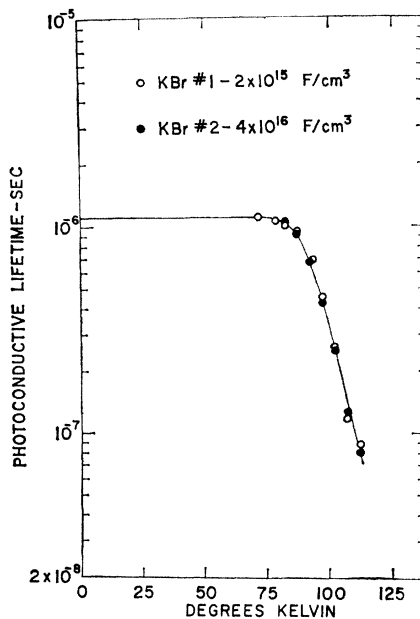


FIG. 7. Photoconductive lifetime vs temperature for two samples of KBr. Field corrections were 1° for sample number 1 and 2° for sample #2. The solid line is a plot of Eq. (1) with $\Delta E = 0.135$ eV, $\tau_R = 1.11 \mu\text{sec}$, and $1/\tau_0 = 1.4 \times 10^{13} \text{sec}^{-1}$.

where g is the degeneracy of the trapping level, and m/m^* is the relative effective mass for the conduction band states. Since the accuracy of determining $1/\tau_0$ is not very high, the value of σ obtained is probably no better than the right order of magnitude. The value obtained for NaCl is particularly uncertain, since only one crystal was examined, and there was considerable evidence of aggregate-center formation in this sample.

IV. DISCUSSION OF RADIATIVE LIFETIME

Smakula¹⁰ has shown that the absorption of the F center may be interpreted semiclassically with an oscillator strength approximately one. Mott and

Gurney¹¹ estimate the lifetime of the inverse process of emission to be $\sim 2 \times 10^{-8}$ sec. A more detailed calculation by Markham⁴ gives 6×10^{-9} sec. This raises the question of how one reconciles these numbers with the observed values, e.g., 6×10^{-7} for KCl. At best, the experimental result is too large by a factor of 30.

There are two possible reasons why the emission process may not be well represented as the inverse of the absorption process: (1) After absorption, the electron may drop into a lower excited (metastable) state. (2) The electron may remain in the same electronic level, but the wave function of the excited state may be drastically altered by the relaxation of the lattice ions.¹ The large Stokes' shift in the fluorescence spectrum suggest that a large lattice relaxation does actually occur. If this results in a very large orbit for the excited state, then the overlap integral between the two states could be reduced after relaxation. If the transition probability can be influenced to such a great extent by the change in the mean value of the configuration coordinate between the excited state and the ground state, this means that the transition probability is very sensitive to the value of the configuration coordinate. Such a state of affairs would cast doubts on methods used for establishing configuration coordinates empirically, for it is ordinarily assumed that the electronic transition probability is independent of the value of the configuration coordinate.¹

Let us consider the alternative possibility (1) of a second excited level being involved. This would presumably be a state having the same parity as the ground state. Since the F center possesses a center of inversion (for the rigid lattice), there will be no transition moment connecting this state to the ground state. This accounts for the lack of any corresponding absorption band. However, there are two ways in which the electron can return to the ground state, both involving the aid of thermal vibrations. In the first way, the center may be raised back up to the level of opposite parity as a result of thermal vibrations. That is, the ratio of the time

TABLE I. Depth of the excited state of the F center below the conduction band, ΔE ; radiative lifetime, τ_R ; frequency factor, $1/\tau_0$; and estimated capture cross section for a negative-ion vacancy or α center.

| Material | Sample | Method ^a | ΔE (eV) | τ_R (μsec) | $1/\tau_0$ (10^{12}sec^{-1}) | σ_a^b (10^{-14}cm^2) |
|----------|----------|---------------------|--------------------|---------------------------------|---|--|
| KCl | 7 | FY | 0.157 | ... | 3.54 ^c | |
| | | FL | 0.145 | 0.565 | 0.96 | |
| | 8 | FY | 0.149 | ... | 4.08 ^c | |
| | | FPL | 0.142 | 0.588 | 1.20 | |
| | | FY | 0.164 | ... | 13.00 ^c | |
| | | FPL | 0.142 | 0.578 | 1.20 | |
| KCl | Average: | | 0.150 | 0.577 | 4.03 | 17 |
| NaCl | 1 | PL | 0.074 | 1.00 | 0.12 | 1.6 |
| KBr | 1,2 | PL | 0.135 | 1.11 | 14.00 | 114 |
| KI | 8 | PL | 0.110 | 2.22 | 3.50 | 36 |

^a FY = fluorescence yield; FL = fluorescence lifetime; FPL = fluorescence and photoconductive lifetime; PL = photoconductive lifetime.

^b Based on the assumption $m = m^*$ and a degeneracy of 2 for the F^* level.

^c Calculated from τ_R/τ_0 , using the value of τ_R obtained from the lifetime data.

¹⁰ A. Smakula, Z. Physik **59**, 603 (1930).

¹¹ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 136.

spent in the upper state to the time spent in the lower state will be proportional to $\exp(-\Delta E'/kT)$ where $\Delta E'$ is a thermal activation energy. Hence, the transition probability would be the transition probability from the upper state multiplied by the above factor. The trouble with this mechanism is that it predicts " $\tau_R \rightarrow \infty$ " at $T \rightarrow 0$. In order to compare with the experimental results, we need a mechanism for emission which can occur at the lowest temperatures.

The other possibility under (1) is that the transition between states of like parity is permitted by a perturbation term in the Hamiltonian which does not have inversion symmetry. This means, in effect, that the eigenstates will no longer have definite parity, i.e., the perturbation will mix nearby states of opposite parity. Then, the matrix element for the radiative transition will be small, but definite. The most logical origin of such a perturbation is in the thermal vibrations of the lattice. Unsymmetrical vibrations will produce a potential energy function which does not possess inversion symmetry. Since the amplitude of such vibrations increases with temperature, τ_R will increase with decreasing temperature, reaching a limiting value at low temperature set by the zero-point vibrations. With τ_R dependent on the temperature, the curves for η_R and τ will not have the same temperature dependence. The effect will be that η_R will saturate below the freeze-in of the ionization, while τ will continue to increase with decreasing temperature until the zero-point vibrations are the only remaining ones. This is in qualitative agreement with the experimental results.

V. RESULTS ON THE INFLUENCE OF M CENTERS

It has been suggested that when M centers are present in a crystal, the energy of an excited F center may be transferred to an M center.¹² This suggestion was based partly on the observation that after a crystal containing only F centers has been exposed to light at room temperature to form M centers, the fluorescence of the remaining F centers is quenched, and M -center luminescence is produced upon illumination with F -band radiation. If this process occurs, and can be interpreted in terms of the simple kinetic model discussed earlier, then one would expect a quenching of the luminescence by M centers to be accompanied by a reduction by the same factor in the yield of photoconductivity, and in the lifetime of the excited state. Several experiments which were carried out for the purpose of testing this hypothesis will now be described.

Figure 8 shows the relative fluorescence yield of a crystal of KCl containing 2×10^{16} F centers/cm³, first after quenching, and then after subsequent exposure to light in the F band at room temperature. The appearance of the high-temperature luminescence characteristic of the M center is seen. If this luminescence is subtracted from the curve at low temperatures, a four-

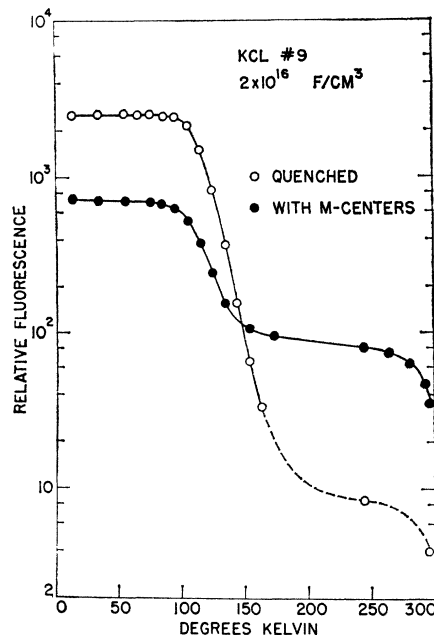


FIG. 8. Relative fluorescence of KCl sample number 9, first after quenching from 600°C, and second after exposure to F band irradiation at room temperature to produce M centers. The M band was undetectable in the first case, while in the second case $\alpha_M/\alpha_F=0.10$.

fold reduction in output is obtained for the low-temperature luminescence to be identified with the F center. The ratio of absorption maxima for the two absorption bands was $\alpha_M/\alpha_F=0.10$ after irradiation.

Figure 9 shows the photoconductivity of the same

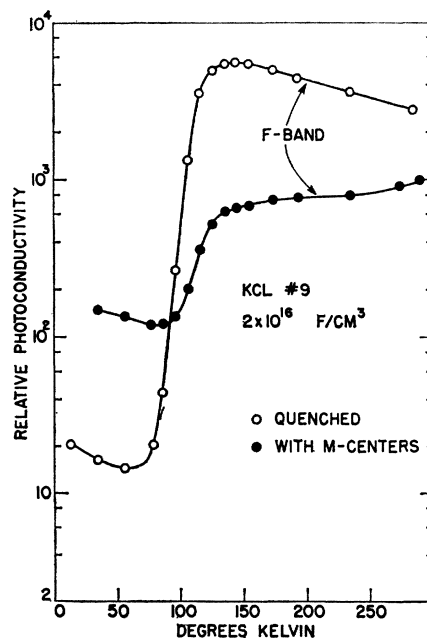


FIG. 9. Photoconductivity of KCl sample number 9 for F band excitation after quenching, and after subsequent irradiation at room temperature to produce M centers. In the second case $\alpha_M/\alpha_F=0.16$.

¹² J. Lambe and W. D. Compton, Phys. Rev. **106**, 684 (1957).

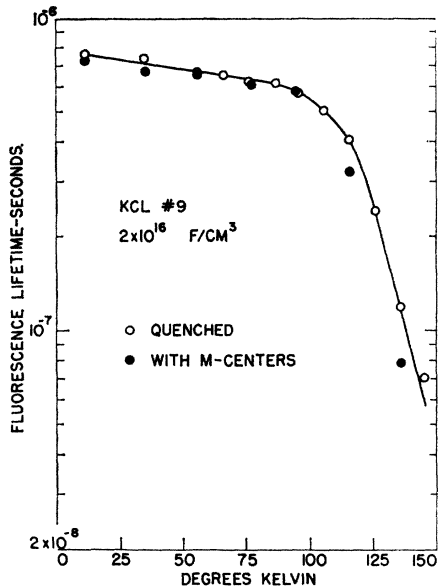


FIG. 10. Lifetime of fluorescence of KCl number 9 under F -band excitation, before and after the production of M centers by exposure to F -band irradiation at room temperature.

sample. The crystal was freshly quenched, after which the M band was again produced by irradiation. In this case $\alpha_M/\alpha_F=0.16$. A drastic change in the whole appearance of the curve is brought about by the production of M centers. Three effects are noted: (1) The low temperature residue is enhanced; (2) the ionization of the F center in the region near the start of the freeze-in ($\sim 150^\circ\text{K}$) has been reduced by a factor of 10; (3) there is a tendency for the loss of photoionization to recover as the temperature is increased. A weak photoconductivity was observed upon irradiation in the vicinity of the M band, as reported by Barth.¹³

The above results clearly show the marked decrease in the ability of the F center to fluoresce and photoionize after M centers are produced by irradiation with F light at room temperature. According to the notion of energy transfer from F centers to M centers, one would expect a similar decrease in the lifetimes.

The lifetimes of fluorescence for this sample before and after the production of M centers is shown in Fig. 10. These measurements were made from the same pulses used in determining the relative fluorescence values given in Fig. 8, so there is no question about the achievement of identical conditions. Contrary to the results of fluorescence and photoconductive yields, the lifetimes show little if any change after M centers are produced.

At high temperatures, where only M center luminescence remains, the lifetime is short, about 6×10^{-8} sec. As the temperature is lowered, the slower F -center component is observed, mixed with the faster M -center

component. At the lowest temperatures, the slow component comprises about 90% of the pulse. In Fig. 10, the lifetimes given are for the slow component only. The highest temperature points are slightly inaccurate because the two components were of comparable magnitude in this region.

Similar observations were made on a sample of KCl containing 3×10^{17} F centers/cm³. At these higher concentrations, a very small M band was evident, even in the quenched sample, whereas after irradiation α_M/α_F was often as high as 0.40. In all cases, irradiation was stopped before an appreciable R_2 band appeared. Under these conditions, the F -center luminescence was essentially zero after irradiation, while the M luminescence was substantial. The lifetime of the latter was found to be 60 nsec and essentially independent of temperature between 100° and 300°K . This result is for excitation in the F band. An attempt to observe the lifetime of M luminescence under M -band excitation was unsuccessful because the emission band was too close to the absorption band.

VI. DISCUSSION OF THE EFFECT OF M CENTERS

The preceding results show clearly that transfer of energy from an excited F center to an M center is not a process which competes with the normal processes of fluorescence and photoionization. If any such transfer takes place, it must happen very quickly, so that in effect those F centers which can transfer energy do so with 100% efficiency, while those which cannot are completely unaffected. This implies that the M center involved would have to be very close to the F center it quenched. In the experiment reported here, one can estimate, that each M center quenched ~ 7 F centers. The reason why so many F centers would cluster about each M center is not clear.

An alternative explanation lies in the assumption that the quenching of F -center fluorescence and ionization is caused, not by the M centers themselves, but by the experimental conditions which produced the M centers. During the irradiation, each F center is photoionized about 100 times. The fact that the F band shrinks only slightly during the whole irradiation is a result of the fact that the electron is nearly always recaptured by an α center to reform a new F center. The α center involved may be one which has just been created through F -center ionization, or it could be one which was already present in the crystal.

We have already seen evidence that α centers are already present in the quenched sample. Suppose that there is a class of α centers which are located in regions of the crystal which are highly disturbed, and suppose that the effect of this environment on the α center is such that when an electron is captured by it, there is a fast, nonradiative conversion from the F^* level to the ground state. Such an effect can be made plausible in

¹³ N. Barth, Z. Physik 149, 370 (1957).

terms of a distortion of the configuration coordinate curves, causing a point of near contact between the ground state and the excited state. Then it is clear that F centers will be formed from these α centers preferentially. Firstly, the effective cross section of these α centers will be greater, because once an electron is captured into the excited state, it will not be re-ionized because of the rapid conversion to the ground state. Secondly, such F centers will be more resistant to bleaching than normal F centers. Hence, in the course of bleaching, there will be a tendency for the F centers to become concentrated in these disturbed regions of the crystal. Whether or not this process, if it takes

place, has a direct bearing on the formation of M centers is a matter of conjecture. However, it can account qualitatively for the results obtained here.

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Magneto-Optical Oscillations in the Free Carrier and Interband Absorption of Semiconductors

E. D. PALIK AND R. F. WALLIS

U. S. Naval Research Laboratory, Washington, D. C.

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In the region of the band edge of a degenerate n -type InSb sample, at fixed wavelength, oscillations in the absorption have been observed which are periodic in $1/H$. The period of these oscillations yields information about the Fermi surface. In the region of free carrier absorption oscillations in the absorption have been observed which are periodic in $1/H$, the period yielding the free carrier effective mass. The two measurements hold promise of an optical means of measuring both carrier concentration and effective mass of free carriers in semiconductors.

1. INTRODUCTION

WHILE measuring the free carrier Voigt effect¹ in n -type InSb at room temperature we noticed that in the transverse orientation, there were small oscillations in the free carrier absorption as the magnetic field was swept. Theoretical work by Gurevich *et al.*^{2,3} led us to investigate the effect more thoroughly. They showed that an oscillatory effect should be observable in the free carrier absorption and the period of the oscillations would yield the free carrier effective mass. We have observed the effect in n -type InSb both at room temperature and more clearly near liquid-nitrogen temperature.

A similar oscillatory effect is observable in the region of the band edge absorption in degenerate semiconductors. This phenomenon was previously observed by Boyle and Rodgers⁴ in bismuth from which they deduced the cross-sectional area of the Fermi surface. We

have observed this effect in n -type InSb containing about 1×10^{18} carriers/cm³ at liquid nitrogen temperature.

2. THEORY

Since the theoretical results given in the two papers of Gurevich *et al.*^{2,3} appear to be inconsistent and since no details of the derivations are given, we prefer to base our discussion on an elementary qualitative theory. We restrict our attention to simple parabolic energy bands.

Turning first to interband absorption, we consider the case of direct transitions from magnetic levels of a simple parabolic valence band with maximum at $\mathbf{k}=0$ to magnetic levels of a simple parabolic conduction band with minimum at $\mathbf{k}=0$. The absorption coefficient in intrinsic material shows maxima for photon energies given by⁵

$$\hbar\omega = E_G + \hbar\omega_{c1}(l + \frac{1}{2}) + \hbar\omega_{v2}(l + \frac{1}{2}), \quad (1)$$

where ω_{c1} and ω_{v2} refer to the conduction and valence band cyclotron frequencies, respectively, and E_G is the energy gap in zero magnetic field.

Let us now consider n -type extrinsic material with carrier concentration N . For simplicity, we take the

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³ L. E. Gurevich, I. P. Ipatova, and Z. I. Uritskii, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 328.

⁴ W. S. Boyle and K. F. Rodgers, Phys. Rev. Letters **2**, 338 (1959).

⁵ E. Burstein, G. S. Picus, R. F. Wallis, and F. Blatt, Phys. Rev. **113**, 15 (1959).