PHYSICAL REVIEW VOLUME 94, NUMBER 6 JUNE 15, 1954

Search for *F*-Center Luminescence

CLIFFORD C. KLICK
Solid State Division, Naval Research Laboratory, Washington, D. C.

(Received February 26, 1954)

Measurements have been made on the quantum efficiency of luminescence from *F* centers in x-rayed LiF and additively colored KCl at 4°K. In the wavelength range from 3000A to 20 000A an upper limit of 3 percent efficiency is found for the LiF *F*-band emission, if it exists. At 25 000A the upper limit is 10 percent. Similar results are found for *F* centers in KCl in the wavelength range from 6500A to 25 000A. These results are in disagreement with theoretical predictions that the *F* center should luminesce with high efficiency in the wavelength region near 10 000A.

INTRODUCTION

THE *F* center in the alkali halides is probably the most widely investigated and best understood imperfection in insulators.[1] It is generally agreed that the *F* center consists of an electron trapped at a negative ion vacancy. Using this model of the *F* center, Gurney and Mott[2] have suggested that absorption in the *F* band raises an electron from the ground state to an excited state and that at high temperatures thermal energy raises the electron from the excited state to the conduction band. This view is supported by several investigations. First, measurements by Glaser and Lehfeldt[3] on the variation of photoconductivity of the *F* center with temperature show a reasonably constant value in the room temperature range followed by a large decrease at low temperatures. Second, Kleinschrod[4] discovered a small absorption band on the high-energy side of the *F*-band absorption. This band may be interpreted as due to a direct transition from the ground state of the *F* center to the conduction band. Finally, Dexter[5] has computed the absorption strength of the *F*-center band and the short wavelength band on the basis of the model of Gurney and Mott and finds agreement with the experimental results of Kleinschrod.

At sufficiently low temperatures then, light absorption in the *F* band raises the electron to an excited state but there is insufficient thermal energy to free the electron. A problem of interest, and the one with which this investigation is concerned, is to determine how the excited *F* center returns to its ground state. If luminescence occurs, as has generally been anticipated,[6] the measurement of the luminescent emission spectrum should yield important information about the relaxation of the lattice around the excited *F* center and allow a determination of configuration coordinate curves for the center from experimental data alone.[7] If, however, there is a radiationless transition of the excited *F* center to its ground state, it will be important to attempt to identify the mechanism for this transition.

Luminescence in alkali halides has been observed in supposedly pure materials under a variety of conditions, such as bombardment by high-energy radiation or heating from low temperatures after x-raying. In most cases, however, the possibility cannot be excluded that the luminescence may arise from impurities since minute concentrations of a large number of metal ions act as luminescent centers in alkali halides,[8] and the reported emission in these cases is frequently of low intensity. In order to avoid the difficulties associated with excitation methods which produce free electrons and holes, the author has previously looked for emission from *F* centers in LiF and NaCl upon irradiating into their absorption bands at 4°K.[9] No emission was found, but the results were limited in the range of wavelengths covered. In addition, no quantitative estimate was made as to the minimum detectable signal in terms of quantum efficiency. Ghormley and Levy[10] have found an emission at 10 000A from colored KCl at 77°K upon exciting with light in the region of the *F*-band absorption. These investigators state, however, that it is not possible to determine from their experiments whether the emission is true *F*-center fluorescence or results from interactions with other centers such as *M* centers. This uncertainty arises from the fact that *M* centers in LiF and NaF are known to luminesce,[11] and that, in the case of LiF at room temperature, irradiation in the *F* band produces a feeble *M*-center luminescence.[9] At 77°K there may be some photoconductivity from *F* centers in KCl, thus permitting the formation or excitation of *M* centers. Also, the range of exciting light used by Ghormley and Levy is sufficiently large so that there may be a small overlap of this light with the *M*-absorption band, thus

---

[1] For reviews of the properties of *F* centers see F. Seitz, Revs. Modern Phys. **18**, 384 (1946), and N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), Chap. IV.

[2] R. W. Gurney and N. F. Mott, Proc. Phys. Soc. (London) **A49**, 32 (1937).

[3] G. Glaser and W. Lehfeldt, Nachr. Akad. Wiss. Göttingen Math. physik. Kl. **2**, 91 (1936).

[4] F. G. Kleinschrod, Ann. Physik **27**, 97 (1936).

[5] D. L. Dexter, Phys. Rev. **83**, 435 (1951).

[6] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), pp. 136, 222.

[7] C. C. Klick, Phys. Rev. **85**, 154 (1952).

[8] It has been found in this laboratory, for instance, that the addition of 40 parts per billion of copper to NaCl causes measurable luminescence.

[9] C. C. Klick, Phys. Rev. **79**, 894 (1950).

[10] J. A. Ghormley and H. A. Levy, J. Phys. Chem. **56**, 548 (1952).

[11] J. P. Molnar, thesis, Physics Department, Massachusetts Institute of Technology (1948) (unpublished).

exciting the M center directly. These investigators do not estimate the quantum efficiency of the luminescence they measure; and, since their experimental measuring technique will detect as little as ten photons per second, they may be measuring a weak or secondary emission.

Theoretical investigations concerning the F center have largely been concerned with the determination of wave functions for the F center and the computation of the F-center absorption band. Recent work by Huang and Rhys[12] considers, in addition, the relative probabilities of radiationless to radiative transitions from the excited to the ground state of the F center. For KBr at a temperature of 28°K they compute this ratio to be 4×10^{-19}. Similar results should be expected for other alkali halides at low temperatures. These figures support the general opinion that the quantum efficiency of luminescence from F centers at low temperatures should be essentially one hundred percent.

There are several ways in which estimates may be made concerning the position of the emission band from F centers. Experience with luminescent centers such as Ag^+, Tl^+, Cu^+, Pb^{++}, and M centers in alkali halides indicates that the ratio of emitted wavelength to absorbed wavelength is less than two.

Pekar[13] has derived relationships between the absorption peak wavelength, the emission peak wavelength, and the half-widths of the peaks for simple centers which may be used to predict the wavelength at which emission from the F center should occur. Using these relations and previous results from a theoretical investigation of F centers,[14] Pekar predicts that luminescence from F centers in NaCl, KCl, KBr, and KI all lie between 9000A and 10 000A. The relations derived by Pekar may have somewhat limited accuracy, however. They predict, for instance, that the half-widths, in energy units, of the absorption and the emission bands are identical, but for KCl:Tl at room temperature the ratio of emission to absorption band width is approximately two.

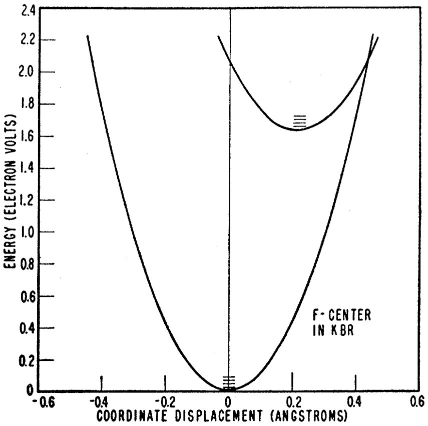

FIG. 1. Configuration coordinate curves for the ground and excited states of the F center in KBr, computed as described in the text. The coordinate is the separation between the F center and a nearest neighbor potassium ion. The horizontal lines indicate the vibrational energy levels of the system as computed. Using cgs units, the energy of the ground state is given by $U_g=1.76\times10^5X^2$, where X is the coordinate displacement; the excited state is given by $U_e=2.61\times10^{-12}+1.5\times10^5(X-0.214\times10^{-8})^2$.

Using both experimental and theoretical results, it is possible to compute the configuration coordinate curves for F centers in KBr, and from these curves determine the emission spectrum. The method used has been described.[7,15] In the case of KBr the data employed are the peak wavelength of absorption, the absorption half-width at low temperatures, the variation of this half-width with temperature,[16] and the number of vibrational quanta given off in absorption as determined theoretically by Huang and Rhys.[12] The effective mass of the system is taken to be that of the six potassium ions surrounding the center. The results of this computation are illustrated in Fig. 1, and from these results the F-center emission would be expected at 12 000A.

EXPERIMENTAL PROCEDURE

For this work LiF and KCl were chosen as the alkali halides to be investigated. LiF has its F band at 2500A, thus allowing an experimental search over an eight to one range of wavelengths from 3000A to 25 000A. However, LiF can be colored conveniently only by x-rays which also produce the full gamut of other color centers. Since the interaction of the F band with other centers was considered unlikely for low F-center concentrations but not impossible, it was felt advisable also to investigate an alkali halide colored by heating in the alkali metal vapor which produces only the F band.

Of the alkali halides which can be conveniently colored by this means, KCl has the shortest wavelength F band and could be investigated over a four to one range of wavelengths. KCl has the added advantage that Pekar has included it as one of the alkali halides for which he predicts F-center luminescence in the wavelength region from 9000A to 10 000A.

Single crystals of LiF, grown commercially, were used. Considerable variation in the luminescent background of untreated crystals was found in various samples from the same producer. Therefore, samples with low background under 2537A excitation were chosen and were colored by exposure to heavily filtered x-rays from a 50-kvp machine. The coloration appeared uniform to the eye. By using Smakula's[17] equation relating the optical absorption to the number of centers

---

[12] K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950).

[13] S. I. Pekar, J. Exptl. Theoret. Phys. (U.S.S.R.) **22**, 641 (1952).

[14] S. I. Pekar, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 510 (1950).

[15] C. C. Vlam has called to our attention an error in the constant of Eq. (4) of reference 7 which is too high by $\sqrt{2}$. Similar corrections should be made in Eqs. (10) and (11) of C. C. Klick and J. H. Schulman, J. Opt. Soc. Am. **42**, 910 (1952).

[16] R. Hilsch and R. W. Pohl, Z. Physik **64**, 606 (1930).

[17] See, for instance, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 662.

and assuming an oscillator strength of unity, the density of *F* centers could be computed. For the samples used in investigating luminescence in the range from 3000A to 6000A, the density was 3.5×10^{17} cm^{-3}; other samples, investigated in the range from 4500A to 26 000A, had a density of 6.6×10^{16} cm^{-3}. These densities correspond, respectively, to concentration of 6 and 1 parts per million of negative ion sites. In each case reported in this investigation the sample thicknesses were such that more than 90 percent of the exciting light was absorbed.

F centers were formed in commercial crystals of KCl by heating in potassium vapor at 450°C. After this treatment the crystals were heated briefly to 600°C and quenched to remove colloid bands. The density of color centers was computed to be 9×10^{16} cm^{-3} using Smakula's equation and an oscillator strength of 0.81. This corresponds to a concentration of 6 parts per million of negative ion sites.

In all cases the alkali halides to be measured were submerged in liquid helium at 4.2K°. The Dewar used was an unsilvered glass double Dewar with the inner Dewar painted black except for a small window at the level of the crystal. The exciting light entered the Dewar vertically through a quartz plate, passed through the liquid helium, and fell on the crystal. When a photomultiplier was used as a detector in the 3000A to 6000A range, it observed the crystal through a second quartz plate placed at the top of the Dewar. When a lead sulfide photoconductive cell was used, the crystals were held at an angle of 45° from the vertical and were observed through the window by the detector placed exterior to the Dewars.

For the investigation of *F* centers in LiF, the exciting source was a low-pressure mercury arc with a Corning 9863 filter. This radiates almost all of its energy in the 2537A mercury line, which falls well within the *F*-center absorption band. In the investigation of KCl, an A-H6 high-pressure 1000-watt mercury arc was used as the exciting source. The light was filtered through a Baird filter 7-2970-3 and Corning filters 4303 and 3484 to pass only light near the *F*-band absorption peak.

A 1P28 photomultiplier tube with a Corning 7740 filter was used to look for luminescence in the range from 3000A to 6000A for LiF *F* centers. For the longer wavelength investigations, an Eastman Kodak lead sulfide cell with dimensions 1 cm by 2 cm was used. For the LiF investigation, no filter was used with the PbS cell other than the filtering action of the Pyrex glass Dewars; for KCl, a Corning 2412 filter was placed before the cell in order to pass only wavelengths greater than 6100A. When the PbS detector was used, the exciting light was chopped at a rate of 10 cycles per second and the detector output amplified by a 10-cycle amplifier. The relative response of both detectors was determined as a function of wavelength by the use of suitable monochromators, chopped light sources, a fast response thermocouple, and an alternating current amplifier.

A measurement of the quantum efficiency of luminescence for some material implies a determination of the number of quanta absorbed by the material and of the number emitted. This involves measurements of the intensity of the exciting light, the fraction of light reflected by the material, the intensity of the emitted light, its angular dependence, and the amount of self absorption of the emitted light by the material. Measurements have been made with fair accuracy on a number of phosphors[18] but it was concluded that the difficulties introduced by the use of complicated Dewars would greatly reduce the accuracy of the measurements. Instead, a substitution method was used in which a material either of known reflectivity or quantum efficiency was substituted for the material to be measured. For LiF in the range where a photomultiplier was used as a detector, the standard was magnesium carbonate for which the reflectivity at 2537A was taken as 72 percent.[19] For the wavelength range in which LiF was investigated with the PbS detector, the standard used was the luminescence of $CaWO_4$. Jones and Fonda[18] give a quantum efficiency at room temperature of 73 percent for this material and Kröger[20] has shown that its brightness increases about 20 percent as the temperature is reduced. It was assumed that this material had a quantum efficiency of 90 percent at 4°K. For the investigation of KCl the standard used was the reflectivity of MgO which was taken to be[19] 95 percent at the wavelength of the *F*-center peak. From the experimentally determined detector responses to these substituted standards, from their known reflectivities or quantum efficiencies and emission spectra, from the measured relative response of the detectors to equal numbers of incident quanta, and from the computed fraction of exciting light absorbed in the sample it was possible to compute at any wavelength what the detector response would be to a material luminescing at this wavelength with an efficiency of 100 percent. Several other corrections have been made to obtain the quantum efficiency data; the fraction of incident light reflected at the front surface of the alkali halide was computed and included in the calculations as was the effect on the angular distribution of luminescent light from a crystal due to refraction at the surface. However, these corrections are of somewhat minor importance in determining the unexpectedly low quantum efficiency.

RESULTS

In no case was efficient *F*-center luminescence found. The results are given in Fig. 2 for both the LiF and

---

[18] S. Jones and G. R. Fonda, Electrochemical Society, enlarged abstract, spring meeting, 1952 (unpublished).

[19] S. Schwartz and G. Lloyd, J. Opt. Soc. Am. **38**, 964 (1948).

[20] F. A. Kröger, Nature **159**, 674 (1947).

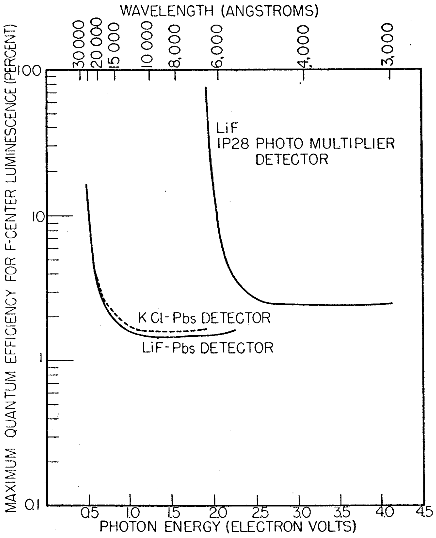

FIG. 2. Experimentally determined upper limit for the quantum efficiency of the *F* centers in LiF and KCl as a function of wavelength. Each point on the curve is computed assuming that the luminescence is concentrated at the wavelength corresponding to the point.

KCl investigations. These curves are obtained by converting the observed detector response, when the colored alkali halide is investigated, into a quantum efficiency at each of various wavelengths by assuming that the detector response is due to *F*-center luminescence concentrated at each wavelength. At wavelengths for which the detector sensitivity is poor, the small observed response corresponds to a higher possible quantum efficiency. The results may be summarized by saying that the efficiency of luminescence of *F* centers in LiF is less than 3 percent if the emission occurs in the wavelength range from 3000A to 20 000A. For KCl the *F*-center luminescence efficiency is less than 3 percent for the range from 6500A to 20 000A. For both materials the efficiency is less than 10 percent at 25 000A. For an emission which extends over a range of wavelengths, the maximum quantum efficiency is given by an appropriately weighted average over this range. If the whole emission spectrum of *F* centers in LiF were included in the range from 3000A to 20 000A, the maximum efficiency would be less than 3 percent.

Because of these low efficiencies no attempt was made to investigate the emission as a function of wavelength; the measurement itself would be difficult and the assignment of apparent emission bands to the *F* center would be open to question because of the possibility of complicating factors such as stray light. In the case of LiF with the photomultiplier detector, for instance, emission from the mercury arc in the 3000A to 4000A range was not filtered from the detector. This is known to be a few percent of the total emission but was tolerated here in order to extend the range of investigation as close as possible to the *F*-center absorption. Similarly with LiF and the PbS detector, some of the red and infrared lines of the mercury arc were not filtered out. Furthermore, there is evidence that excitation in the *F* center leads to weak luminescence in the *M* center. Finally there are the effects of small concentrations of impurities which frequently are troublesome in visible and ultraviolet emission investigations and which might also give rise to infrared emission.

Considering all of these difficulties which arise when such low light levels are investigated, it is possible that the efficiency of luminescence of the *F* center itself is really much less than that given in Fig. 2; these curves should be taken only as upper limits of the efficiency.

DISCUSSION

This investigation indicates that within the rather wide wavelength range investigated, the luminescence of the *F* center, if it exists at all, is one to two orders of magnitude less than expected. Two possible explanations may be examined.

First, the concentration of color centers may be so high that the luminescence is quenched. This phenomenon is well known in phosphors but begins to occur at concentrations above 100 parts per million even in materials with high dielectric constants such as the sulfides. In KCl:Tl the efficiency has decreased less than a factor of 2 because of concentration quenching even at concentrations of 7000 parts per million. Theory[21] also indicates that this effect should become important at concentrations of 1000 parts per million. Therefore the low *F*-center concentrations used here, less than 10 parts per million, avoid this difficulty.

Second, the luminescence may not appear because of the presence of "poisons." In nonphotoconducting phosphors the effect of poisons in concentrations as low as 10 parts per million may be detected. The mechanism for efficient poisoning is probably that of dipole-dipole transfer of energy discussed by Dexter[22] who concludes that concentrations of the order of 100 parts per million are required and that the poison should have an allowed absorptive transition in the wavelength range of the emission which it quenches. Therefore a poison should have a large oscillator strength and even in concentrations of only 10 parts per million should show an absorption band comparable with the *F* bands investigated here. No such bands were found nor does there appear to be any reference in the literature to such effects.

The conclusion then appears to be that current

---

[21] D. L. Dexter and J. H. Schulman (to be published).

[22] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

F-center theory, which predicts luminescence near 10 000A with 100 percent efficiency, is not correct. It is possible that a more detailed theoretical investigation of the configuration coordinate curves for the *F* center, both in its ground state and in its excited state, might lead to a better understanding of these results.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of Robert J. Ginther in preparation of the materials and of Clifford J. Grebenkemper in supplying the liquid helium; the author is especially indebted to Dr. David L. Dexter and Dr. James H. Schulman for numerous discussions of this work.

PHYSICAL REVIEW VOLUME 94, NUMBER 6 JUNE 15, 1954

Theory of Thermodielectric Effect

B. Gross
Instituto Nacional de Tecnologia, Rio de Janeiro, Brazil

(Received July 13, 1953; revised manuscript received October 26, 1953)

A theory is put forth to explain the electrical effects which accompany phase changes occurring in dielectrics and aqueous solutions. Ionic movement in the interface is treated as a transition between energy levels separated by potential barriers. The height of the barriers and the value of the energy levels are supposed to be different for positive and negative ions. Such a model results in a net current flow across the solid-liquid interface. When the interface moves during a phase change of the system, the excess electric charges thus produced constitute space charges in the solid and surface charges in the liquid. The field of the global charge distribution causes the appearance of the currents and potential differences which have been observed between the plates of a condenser containing the dielectric.

INTRODUCTION

COSTA RIBEIRO, a Brazilian physicist, while studying electret behavior and related effects, discovered in 1944 that solidification and melting of many dielectrics are accompanied by charge separation.[1] He found that the phenomenon is observed only if the phase change proceeds in an orderly fashion, that is, if a definite phase boundary (or interface) exists between the solid and liquid phase. Displacement of the interface in one direction corresponds to solidification, and displacement in the opposite direction to melting. A system in which such a process occurs, has properties similar to those of a primary cell with very high internal resistance. Measurements were made of the short circuit current and the total charge separation. The first observations concerned dielectrics like carnauba wax, naphthalene (where the effect is particularly strong), and paraffin; however, occurrence in ice was also mentioned. Costa Ribeiro concluded that the effect was a general one: Production of currents and charge separation in dielectrics during phase changes. Later Workman and Reynolds[2] and Alfrey and Gill[3] found that orderly solidification of many aqueous solutions gives rise to the appearance of considerable open-circuit potentials (of the order of hundreds of volts) which become measurable when the freezing is observed inside a condenser in open circuit. These authors also give astonishingly high values for the total charge separation in aqueous solutions, and this was thought to be significant for the interpretation of atmospheric electricity. For this reason the effect, besides its theoretical interest, is likely to become of practical importance. Recently Krause and Renninger[4] found that individual crystals of pentaerythren become electrically charged during crystallization from a supersaturated solution. Numerous other papers have been published since 1944 on similar matters, partly in continuation of the previously mentioned ones,[5] partly independently.[6] It is also worth mentioning that as early as 1940 some observations along the same line were reported in meteorological papers.[7] It has already been asserted that the findings of Costa Ribeiro and Workman and Reynolds refer to the same effect[8] as does, in the author's opinion, the evidence contained in all previously mentioned papers. It is therefore justified to call

---

[1] J. Costa Ribeiro, thesis, Universidade do Brasil, 1945; Anais acad. brasil. cienc. **17**, No. 2, 2, 3 (1945); **22**, 321 (1950).

[2] E. J. Workman and S. E. Reynolds, Phys. Rev. **74**, 709 (1948); **78**, 254 (1950).

[3] E. W. B. Gill and S. A. Alfrey, Nature **169**, 203 (1952); E. W. B. Gill, Nature **169**, 1109 (1952); Brit. J. Appl. Phys. Supplement 2, 16 (1953).

[4] B. Krause and M. Renninger, Naturwiss. **40**, 52 (1953).

[5] J. Costa Ribeiro, Abstracts of Simposio sobre Novas Técnicas da Física, Rio de Janeiro, 1952 (unpublished), p. 23; L. Cintra do Prado, Anais acad. brasil. cienc. **18**, 145, 149 (1946); L. Cintra do Prado and P. Saraiva, Anais acad. brasil. cienc. **19**, 30 (1947); P. Saraiva, Anais acad. brasil. cienc. **18**, 161 (1946); A. Dias Travares, Anais acad. brasil. cienc. **25**, 53, 91 (1953).

[6] I. Clay and C. Kramer, Physica **13**, 508 (1947); A. Becker and I. Schaper, Z. Naturforsch. **4a**, 194 (1949); W. Rau, Z. Naturforsch. **6a**, 649 (1951); V. J. Schaefer, Phys. Rev. **77**, 721 (1950).

[7] W. Findeisen, Z. Meteorol. **57**, 6, 201 (1940); E. Lange, Z. Meteorol. **57**, 12, 429 (1940); A. Klumm, Arch. Meteorol., Geophys. u. Bioklimatol., Ser. **A3**, 382 (1951).

[8] J. D. Hoffman, Dig. of Lit. Dielectrics (Nat. Research Council) **14**, 13 (1950).