

Electric-Field Ionization of the Excited F Center in $KCl\ddagger$

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Following Lüty's original observations that excited F centers could be ionized by applied electric fields, Euwema and Smoluchowski calculated the probabilities for two effects, a low-temperature tunneling effect and a higher temperature Schottky effect. In this paper we extend the Euwema-Smoluchowski theory and report on luminescence measurements of both effects for the KCl F center. The results are analyzed on the basis of the "large-orbit" picture of the relaxed excited state developed by Fowler. The Schottky data fit the theory very well, yielding an effective dielectric constant about equal to the static dielectric constant. The tunneling data are in qualitative agreement with theory.

I. INTRODUCTION

THE nature of the excited F center after lattice relaxation has been the subject of considerable recent interest.¹⁻⁷ Because of the absence of luminescence data, little was known about the relaxed excited F center for many years. Since the first observation of F -center luminescence⁸ and the subsequent measurement of many of its properties it has become clear that the F center in emission differs in a number of ways from the F center in absorption. For example, the peak energy of emission is typically about half that of absorption^{8,9} and the radiative lifetime is at least an order of magnitude larger than one would expect from simple considerations based on the absorption strengths.^{1,2}

It was first shown experimentally by Lüty¹⁰ in 1958 that excited F centers could be ionized by applied electric fields. He observed a temperature- and field-dependent ionization at temperatures above 63°K. Although Lüty first attributed this ionization to a quantum-mechanical tunneling process, he and Euwema and Smoluchowski¹¹ (hereafter referred to as ES) later pointed out that in fact what was observed at these relatively high temperatures was a Schottky effect, that is, thermally-activated ionization due to a lowering of the height of the potential barrier by the applied

field. Fedders and Lüty have also measured a low-temperature field ionization which is temperature-independent.^{11,12} This most likely *does* result from tunneling. ES indicated the analytical form of the Schottky effect, and in addition presented a theoretical analysis of the expected behavior of a hydrogenic F center with respect to field-induced tunneling.

Recently, one of us developed a theory of the relaxed excited F center,⁷ an important result of which is that the relaxed $2p$ state has a large orbit of at least 4 to 5 nearest-neighbor distances. Such a state is quite close to being hydrogenic, in contrast to the $2p$ state in absorption which has a rather compact wave function. This result indicates that the analysis of ES may fit the situation rather well, and allow us to determine certain parameters associated with the relaxed excited state of the F center and compare them with theory.

We thus undertook a measurement of the lifetime and of the quantum yield of luminescence as a function of temperature and electric field for the excited state of the KCl F center. Both the high-temperature Schottky effect and the low-temperature tunneling effect were studied. We then analyzed the results on the basis of a hydrogenic model. In Sec. II a discussion of the theory is presented, with certain extensions of the ES treatment included. Section III contains a description of the experiment and an analysis of the data, while Sec. IV consists of a summary and conclusions.

II. THEORY

The purpose of this section is twofold: first, to discuss and extend the ES treatment of field ionization for the perfect hydrogenic impurity, and second, to discuss the application of the derived results to the case of the relaxed F center.

A. Perfect Hydrogenic Impurity

1. Tunneling

A theory for the quantum-mechanical tunneling of an electron from a hydrogen-like atom due to an applied

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¹ R. K. Swank and F. C. Brown, Phys. Rev. Letters 8, 10 (1962); Phys. Rev. 130, 34 (1963).

² W. Beall Fowler and D. L. Dexter, Phys. Rev. 128, 2154 (1962).

³ W. Beall Fowler and D. L. Dexter, Phys. Stat. Solidi 3, 1865 (1963).

⁴ G. Spinolo and F. C. Brown, Phys. Rev. 135, A450 (1964).

⁵ G. Spinolo, Phys. Rev. 138, A1495 (1965).

⁶ R. F. Wood and H. W. Joy, Phys. Rev. 136, A451 (1964).

⁷ W. Beall Fowler, Phys. Rev. 135, A1725 (1964).

⁸ Th. P. I. Botden, C. Z. van Doorn, and Y. Haven, Philips Res. Rept. 9, 469 (1954).

⁹ J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962).

¹⁰ F. Lüty, Z. Physik 153, 247 (1958); *Halbleiterprobleme* (Friedrich Vieweg und Sohn, Braunschweig, 1960), Vol. VI, p. 276.

¹¹ R. N. Euwema and R. Smoluchowski, Phys. Rev. 133, A1724 (1964).

¹² H. Fedders and F. Lüty (private communication).

electric field was outlined by Bethe and Salpeter.¹³ Landau and Lifshitz¹⁴ presented a calculation for tunneling from the ground state of such an atom. Perhaps the first application of these ideas to the impurity problem was made by Franz and Tewordt,¹⁵ who considered tunneling by an effective-mass electron from a 1s impurity state in a semiconductor. Perlin and Cheban¹⁶ performed a calculation of impurity-center ionization, and ES utilized Bethe and Salpeter's formalism in connection with the F -center problem. All of these treatments are based on the WKB approximation.

As ES have pointed out, the probability of the electron's tunneling from a hydrogenic atom under an electric field ϵ applied in the z direction is

$$\frac{1}{\tau_\epsilon} = \frac{\exp[-2\int_{\eta_i}^{\eta_f} (|\Phi(\eta)|)^{1/2} d\eta]}{4\int_{\eta_i}^{\eta_0} (|\Phi(\eta)|)^{-1/2} d\eta}, \quad (1)$$

where

$$\Phi(\eta) = -\frac{1}{2}m^*E + m^*\beta_1/\eta d - [(m^2-1)/4\eta^2] + \frac{1}{4}m^*\epsilon\eta. \quad (2)$$

In Eqs. (1) and (2), $\eta = r - z$ is a parabolic coordinate, d is an effective dielectric constant, E is the magnitude of the binding energy, and m and β_1 are related to the parabolic quantum numbers. η_i and η_0 represent the classically permitted interior region for the electron, η_f the beginning of the classically permitted exterior region. We have generalized the ES treatment by including a (scalar) effective mass m^* . Atomic units are used throughout except where otherwise noted.

Let us consider the $n=2$ level, which is the one of interest for the F center. With no external fields there are 4 degenerate orbital states, which we may denote by s, z, x, y (in the case of the F center, of course, we expect at least some of this degeneracy to be removed). Upon application of the field the appropriate linear combinations are (1) = $(1/\sqrt{2})(s+z)$, (2) = $(1/\sqrt{2})(s-z)$, x, y . States (1) and (2) are split apart symmetrically from the states x, y which remain degenerate. Somewhat surprisingly state (2), which is the lowest in energy, will be the state ionized first since its wave function is concentrated in the η direction from which tunneling is most likely to occur. In the picturesque language of Condon and Shortley,¹⁷ the electron in this state is "reckless and wastrel, hurling itself against a less leaky barrier often enough to rob itself of the chance to shine!" State (2) will have quantum numbers $\beta_1 = \frac{3}{4}$, $m=0$. The next states to be ionized (x, y) have $\beta_1 = \frac{1}{2}$, $m = \pm 1$, while state (1) has $\beta_1 = \frac{1}{4}$, $m=0$. To

¹³ H. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), Sec. 54.

¹⁴ L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), pp. 257-258.

¹⁵ W. Franz and L. Tewordt, *Halbleiterprobleme* (Friedrich Vieweg und Sohn, Braunschweig, 1956), Vol. III, p. 1.

¹⁶ Yu. E. Perlin and A. G. Cheban, *Fiz. Tverd. Tela* 4, 3220 (1962) [English transl.: *Soviet Phys.—Solid State* 4, 2358 (1963)].

¹⁷ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), p. 409.

evaluate the tunneling probability for a given state, then, one merely substitutes the appropriate quantum numbers into Eq. (2), finds the zeros of $\Phi(\eta)$ (thereby determining η_i, η_0, η_f), and evaluates Eq. (1) for $1/\tau_\epsilon$. ES have evaluated the numerator of the right-hand side of Eq. (1) for the states x, y . They have also estimated the size of the denominator, assuming that in the case of the F center it represents an integral over the potential well. In the hydrogenic model the denominator may be evaluated directly, however; by letting $\eta_i=0$ and making the substitution $\eta = \eta_0 u$, one may show that for the x, y states

$$4 \int_{\eta_i}^{\eta_0} (|\Phi(\eta)|)^{-1/2} d\eta = \frac{4}{d(m^*)^{1/2}} \left(\frac{2}{E}\right)^{3/2} (1+\kappa)^{3/2} \left[\frac{\mathbf{K}(\kappa) - \mathbf{E}(\kappa)}{\kappa} \right], \quad (3)$$

where the quantities have been defined by ES and are as follows:

$$\epsilon/\epsilon_{cl} = 4\kappa/(1+\kappa)^2, \quad (4)$$

where ϵ_{cl} , the classical field necessary for ionization, equals $\frac{1}{2}E^2d$;

$$\eta_0 = (1+\kappa)/Ed, \quad \eta_f = \eta_0/\kappa, \quad (5)$$

and $\mathbf{K}(\kappa), \mathbf{E}(\kappa)$ are complete elliptic integrals. Thus the tunneling probability from the x and y states is

$$\frac{1}{\tau_\epsilon} = \frac{(m^*)^{1/2} \times 4.13 \times 10^{16-F(\kappa)} E^{-1/2} d^{-1} (m^*)^{1/2}}{(4/d)(2/E)^{3/2} (1+\kappa)^{3/2} \mathbf{D}(\kappa)}, \quad (6)$$

where the function $F(\kappa)$, defined by ES, is given by

$$F(\kappa) = 0.409\kappa^{-1}(1+\kappa)^{1/2} \times [(1+\kappa)\mathbf{E}(1-\kappa) - 2\kappa\mathbf{K}(1-\kappa)] \quad (7)$$

and

$$\mathbf{D}(\kappa) = (\mathbf{K}(\kappa) - \mathbf{E}(\kappa))/\kappa. \quad (8)$$

So much for the transverse states. We have extended the ES analysis to the case of longitudinal states, those with dipole moment parallel to the applied field. We made one key assumption, which makes the analysis completely analogous to that of ES; we assumed that we could neglect the term $1/4\eta^2$ in Eq. (2). Since in application to the F -center problem typical values of η are from 30 to 150 Bohr radii, this assumption is a good one. The results then are as follows: for the state (2)

$$\epsilon_{cl} = E^2d/3 \quad (9)$$

and

$$\frac{1}{\tau_\epsilon} = \frac{(m^*)^{1/2} \times 4.13 \times 10^{16-1.5F(\kappa)} E^{-1/2} d^{-1} (m^*)^{1/2}}{(6/d)(2/E)^{3/2} (1+\kappa)^{3/2} \mathbf{D}(\kappa)} \quad (10)$$

and for the state (1)

$$\epsilon_{cl} = E^2d \quad (11)$$

and

$$\frac{1}{\tau_\epsilon} = \frac{(m^*)^{1/2} \times 4.13 \times 10^{16-0.5F(\kappa)E^{-1/2d-1}(m^*)^{1/2}}}{(2/d)(2/E)^{3/2}(1+\kappa)^{3/2}\mathbf{D}(\kappa)}. \quad (12)$$

2. Schottky Effect

We define a quantity $\Phi'(\eta)$ equal to $2\Phi(\eta)/m^*$, where $\Phi(\eta)$ is given in Eq. (2). Then

$$\Phi'(\eta) = -E + \frac{2\beta_1}{\eta d} - \frac{2}{m^*} \left[\frac{m^2 - 1}{4\eta^2} \right] + \frac{1}{2}\epsilon\eta. \quad (13)$$

The energy function $\Phi'(\eta)$ determines the height of the barrier which the electron must surmount to escape, i.e., the thermal activation energy. For $\epsilon=0$ the change in $\Phi'(\eta)$ between $\eta_0[\Phi'(\eta_0)=0]$ and the value of η for which $\Phi'(\eta)$ is a maximum ($\eta=\infty$) is $-E$. For $\epsilon \neq 0$ the value of η corresponding to $|\Phi'|_{\max}$ changes as does $|\Phi'|_{\max}$; we find as in the preceding section that the term $(2/m^*)[(m^2-1)/4\eta^2]$ may be neglected. The changes in barrier heights for the states of interest are: state (2), $(3\epsilon/d)^{1/2}$; states x, y , $(2\epsilon/d)^{1/2}$; state (1), $(\epsilon/d)^{1/2}$. The result for x, y is the same as that presented by ES.

B. Application to the F Center

In order to apply the foregoing considerations to the case of the F center it is necessary to make a number of assumptions and approximations, all of which are to some degree arbitrary.

The foremost assumption is that the picture which emerges from Fowler's calculation⁷ of the relaxed excited F center is valid, and that the $2p$ state in question has a large orbit and behaves hydrogenically with an effective mass m^* and an effective dielectric constant d . Thus the present experiments may be regarded to some extent as tests of this model for the relaxed excited state.

We assume that the core correction to the F -center potential and any long-range behavior which is non-Coulombic will be effects sufficiently small that the Schrödinger equation may be separated in parabolic coordinates without large error. This statement means that an effective-mass approximation (with a scalar mass) may be made and that any diabatic aspects of the problem will not affect the separation or the definition of the dielectric constant d .

While making the foregoing assumptions we shall allow for the fact that the relaxed $2p$ and $2s$ states are probably nondegenerate, at least in some cases. Although it is very difficult to perform an accurate calculation of the difference in energy between these states, rough estimates indicate that in the absence of external fields the $2s$ state will lie above the $2p$ level (in KCl or NaCl) by at least a few hundredths of an eV. This may not be true for F centers with very small binding energy, such as in CsBr,⁵ but for the case at hand we shall proceed under the assumption that the

$2s$ state is sufficiently separated from the $2p$ that there is not an appreciable mixing of the two.¹⁸

Thus we assume that even under the influence of the applied field the three $2p$ states (x, y, z) will remain nearly degenerate. There next arises another question: How will these states be populated during lattice relaxation, and what is the probability of reorientation after relaxation? It is known that in the absence of an electric field one cannot obtain polarized F -center luminescence¹⁹; thus, the 3 states are populated equally during the $\approx 10^{-6}$ sec after absorption and before emission. It is quite possible that this distribution is achieved during the lattice relaxation which occurs in $\approx 10^{-12}$ – 10^{-10} sec after absorption.

After relaxation there is expected to be some Jahn-Teller splitting which will tend to stabilize a particular p state against reorientation; on the other hand, there may well be phonons available which will tend to cause reorientation. If there is rapid and continual reorientation of the p states after relaxation, the lifetime of the level will be determined by the state whose lifetime is shortest; if, on the other hand, the states do not reorient, each one will decay in its characteristic way independent of the other.

In the absence of clearcut evidence in favor of either of these hypotheses, we shall assume that a good approximation to the time dependence of the processes may be obtained by studying the x and y states only. We do not know the ionization probability for the z -like state, but it will certainly be smaller than that for the state (2) which would exist in the purely hydrogenic case. Thus decay of the z state may well occur at about the same rate as that of the x and y states. Experimentally we observe luminescence originating from the x and y states, and we then analyze it, assuming that either (a) it is independent of the luminescence from the z state, or (b) it has about the same decay properties as the luminescence from the z state.

One may note parenthetically that for the hydrogen atom the various p states are apparently stable against reorientation. The emission lines associated with the most easily ionized state disappear first in an electric field, whereas other lines remain¹³; if the most easily ionized states were continually being populated, the entire spectrum for a particular level would disappear.

III. EXPERIMENT AND ANALYSIS OF THE DATA

A. Experimental Details

Harshaw crystals were used in the experiment. They were colored at room temperature to a density ranging

¹⁸ The matrix element of $-eez$ between hydrogenic $2p_z$ and $2s$ states is equal to $3d\epsilon/m^*$. The maximum value of ϵ applied in our experiment is $\approx 2 \times 10^5$ V/cm = 3.9×10^{-5} a.u.; using $d=4$ and $m^*=0.6$, the matrix element equals 0.022 eV. Since this is of the same order of magnitude as the estimated zero-order $2s-2p_z$ splitting, little mixing of the states or further splitting will arise.

¹⁹ C. C. Klick and W. D. Compton, J. Phys. Chem. Solids **7**, 170 (1958).

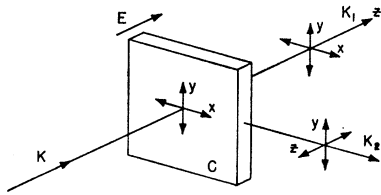


FIG. 1. Geometry of the electric-field experiment. The crystal C is placed in an electric field E which is applied in the z direction. The exciting light of wave vector K (in the z direction) has its electric field in the xy plane. Light may be emitted in any of several directions, including K_1 and K_2 . In the present experiment light emitted in the z direction (K_1) is observed, with electric vector in the xy plane.

from 6×10^{15} to 9×10^{16} F centers/cm³ with x rays from a Norelco MG 150 tube with a 0.1-mm copper filter. The crystal thickness was about 0.5 mm.

After coloration the specimens were located under safety light in an optical cryostat between two electrodes made of fine mesh (supplied by Buckbee Mears Company, St. Paul, Minnesota). One of these electrodes was silver-painted in such a way as to cover the hole of the crystal holder and the other was connected to the dc high-voltage power supply. The geometry was such that the electric field was perpendicular to the electric vector of the observed luminescence (see Fig. 1). The experiment with field and polarization of the luminescence in the same direction proved to be extremely difficult to perform.

Thermal contact of the crystals with the holder was obtained through light spring tension of the insulating support of the high-voltage electrode. The voltage was applied at liquid He temperature to avoid ionic polarization effects. In obtaining Schottky effect data the different temperatures were achieved by simply letting the crystal holder warm up after the liquid helium completely evaporated.

For exciting the luminescence we used a fast, high-intensity nitrogen spark,¹ choosing the proper band with Corning filters. In detection another Corning filter excluded the exciting light from the RCA-7102 photomultiplier. The signal from the photomultiplier was sent through a cathode follower to an amplifier and then to the oscilloscope on whose screen it was photographed. The pulse-analysis technique has been described elsewhere.^{1,4}

B. The Data and Their Analysis

The lifetime of the excited state may be written as a sum of individual terms as follows¹:

$$\frac{1}{\tau} = \frac{1}{\tau_R} + \frac{1}{\tau_Q} + \frac{1}{\tau_0} e^{-\Delta E/kT} + \frac{1}{\tau_\epsilon} \quad (14)$$

In Eq. (14), $1/\tau_\epsilon$ is the tunneling probability; $(1/\tau_0)e^{-\Delta E/kT}$ is the probability of escape over the barrier ΔE ; $1/\tau_R$ is the spontaneous emission proba-

bility, and $1/\tau_Q$ is the probability of any other process which could lead to decay of the state. We assume that $1/\tau_\epsilon$ is given by Eq. (6), while

$$\Delta E = E_0 - (2\epsilon/d)^{1/2}, \quad (15)$$

where E_0 is the thermal depth of the excited state below the conduction band (discussed by Mott and Gurney²⁰ and measured by, among others, Swank and Brown¹).

The quantum efficiency for luminescence is defined by

$$\eta_R = \tau/\tau_R, \quad (16)$$

and one may easily show that

$$(1 - \eta_R) = \frac{1}{\tau} + \frac{1}{\tau_\epsilon} + \frac{1}{\tau_0} e^{-\Delta E/kT} + \frac{1}{\tau_Q}. \quad (17)$$

When the Schottky experiment is performed, the applied fields are sufficiently small that $1/\tau_\epsilon$ is negligible; when the tunneling experiment is performed the temperature is sufficiently low that the Schottky term [the second term in Eq. (17)] is negligible. Thus we may determine these probabilities separately, along with any $1/\tau_Q$.

In the following analysis we shall work with Eqs. (16) and (17), which treat together the quantum yield and lifetime data. In previous work these data have been analyzed separately.¹ We feel that the present procedure has some advantage: Eq. (16) tells us directly whether or not τ_R varies with the parameters T or ϵ , while Eq. (17) tells us directly whether or not there is a $1/\tau_Q$ term.

TABLE I. Data obtained in Schottky experiment on KCl. (a) ϵ is 7.7×10^4 V/cm and T is varied. η_R is the quantum yield of luminescence, τ the lifetime, τ_R the radiative lifetime of the excited state. (b) T is 77°K and ϵ is varied.

(a) $10^8/T$	η_R	$10^{-6}/\tau$ sec ⁻¹	$(1 - \eta_R)10^{-6}/\tau$ sec ⁻¹	$\eta_R \times \frac{10^{-6}}{\tau} = \frac{10^{-6}}{\tau_R}$ sec ⁻¹
10.7	0.204	8.0	6.37	1.63
11.2	0.232	6.0	4.61	1.39
11.8	0.417	3.8	2.22	1.58
12.1	0.476	2.95	1.55	1.41
12.8	0.629	2.50	0.93	1.57
13.6	0.718	2.15	0.61	1.54
14.4	0.741	2.10	0.54	1.56
16.1	0.800	1.95	0.39	1.56
17.5	0.877	1.85	0.23	1.62
				Average = 1.54
(b) $\sqrt{\epsilon} \times 10^8$ a.u.	η_R	$10^{-6}/\tau$ sec ⁻¹	$(1 - \eta_R)10^{-6}/\tau$ sec ⁻¹	$\eta_R \times \frac{10^{-6}}{\tau} = \frac{10^{-6}}{\tau_R}$ sec ⁻¹
0.355	0.769	2.15	0.52	1.63
0.385	0.675	2.45	0.80	1.65
0.415	0.555	2.85	1.27	1.58
0.440	0.357	3.10	1.99	1.11
0.455	0.318	3.80	2.59	1.21

²⁰ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (The Clarendon Press, Oxford, 1948), 2nd ed., pp. 136-137.

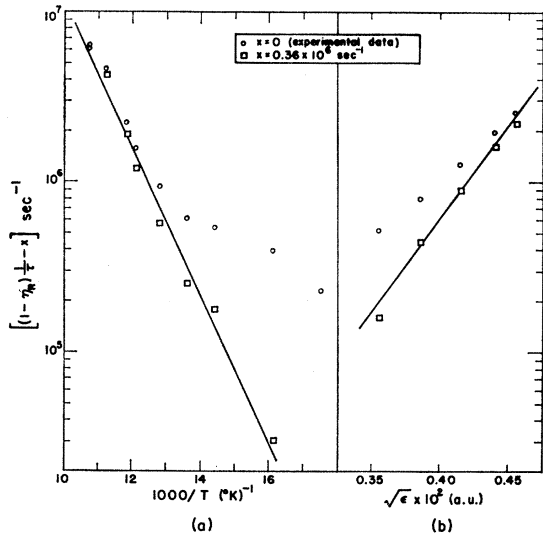


FIG. 2. Plot of Schottky data for KCl F centers. For (a) ϵ equals 7.7×10^4 V/cm, while for (b) T equals 77°K .

C. Schottky Experiment

The Schottky experiment was performed in two ways: by varying the field while the temperature was held constant, and by varying the temperature while the field was held constant. In Table I these are listed pertinent data obtained in this experiment for KCl. In Fig. 2 we have plotted in curve (a) $\ln[(1-\eta_R)/\tau]$ versus $1/T$, with ϵ equal to 7.7×10^4 V/cm, and in (b) $\ln[(1-\eta_R)/\tau]$ versus $\epsilon^{1/2}$, with T equal to 77°K . The F -center concentration was $\approx 7 \times 10^{15}$ cm $^{-3}$. One may notice that the plot (a) does not yield a straight line, as it should if $1/\tau_Q$ were zero. If we assume a constant $1/\tau_Q$ equal to 0.36×10^6 sec $^{-1}$ and plot $\ln[(1-\eta_R)/\tau - 1/\tau_Q]$, the second set of points in (a) obtains, which may be fit with a straight line of slope such that d equals 4.4 and $1/\tau_0$ equals 0.56×10^{12} sec $^{-1}$ [assuming that E_0 is 0.16 eV and that ΔE is given by Eq. (15)].

In (b) we show both the original data and $\ln[(1-\eta_R)/\tau - 1/\tau_Q]$ plotted versus $\epsilon^{1/2}$. This curve yields a value of d equal to 5.0 and a $1/\tau_0$ of 0.55×10^{12} sec $^{-1}$.

One may observe any temperature or field dependence of τ_R by noting its computed value, Table I. Although there is some scatter in values, there appears to be no temperature dependence in the temperature range observed, but there does appear to be some field dependence for higher fields. Whether this is a real effect or whether it arises from difficulties in determining lifetimes in this range of τ is not completely clear.

One may also note that we have assumed that the effective electric field at the center is equal to the applied field. Although this is not expected to be the case for a very localized center (such as the F center in its ground state) it should be a good assumption for the diffuse excited state.⁷

The results obtained by varying T and ϵ are in quite good agreement with each other (this could probably be improved somewhat by using a slightly different value for E_0). The important fact that emerges is that the resulting values of d are large, of the order of the static dielectric constant; thus they are in agreement with the large-orbit picture of the relaxed excited F center.⁷

There is not a great deal that can be said about $1/\tau_Q$, except that it must actually be a slowly varying function of temperature and/or field. Since we do not measure η_R absolutely, all our values are referred to that for $T=0$, $\epsilon=0$. If $1/\tau_Q$ were independent of T and ϵ it would not show up in our analysis. We believe that this "extra" term is in fact the same as has been observed by Swank and Brown¹ in F -center luminescence and by Spinolo and Brown⁴ in F_A -center luminescence. If so, it must be a function at least of T . Several possibilities for its origin include the following: (1) an extra temperature dependence in $1/\tau_0$ or in ΔE (possibly related to thermal lattice expansion); (2) some thermally activated process involving the $2s$ state; (3) a nonradiative transition to the ground state. Analysis of some of Swank and Brown's data indicates that their "extra" low-temperature effect can be fitted by a Boltzmann-type term with an activation energy of the order of thousandths of an eV.

D. Tunneling Experiment

The tunneling experiments were performed on KCl at liquid-helium temperatures. Again lifetimes and quantum yields were measured. Typical results are listed in Table II.

Before discussing the detailed analysis of these data it is worthwhile to call attention to several points. τ varies more slowly with field than does η_R , which implies that τ_R is a function of the field; as indicated, $1/\tau_R$ computed from Eq. (16) varies from 1.64×10^6 sec $^{-1}$ to 0.82×10^6 sec $^{-1}$ as ϵ varies from zero to 1.98×10^5 V/cm. This variation of τ_R is probably a real effect. The applied field tends to increase η_0 , the interior dimension of the relaxed excited state; according to Fowler⁷ the ground state is very compact and the dipole matrix element with the excited state is a rather strong function of the size of the excited state. This points up the im-

TABLE II. Variation of lifetime and quantum yield for KCl F centers at 4°K as a function of applied field. The F -center concentration is 6×10^{15} cm $^{-3}$.

$\epsilon \times 10^{-5}$ V/cm	η_R	$1/\tau \times 10^{-6}$ sec $^{-1}$	$\frac{10^{-6}}{\tau} = \frac{10^{-6}}{\tau_R}$		$(1-\eta_R) \frac{10^{-6}}{\tau}$ sec $^{-1}$
			η_R	τ_R	
0	1	1.64	1.64	0	0
1.21	0.885	1.82	1.61	0.21	0.21
1.46	0.835	1.78	1.49	0.29	0.29
1.64	0.695	2.12	1.47	0.65	0.65
1.75	0.550	2.27	1.25	1.02	1.02
1.88	0.450	2.04	0.92	1.12	1.12
1.98	0.345	2.38	0.82	1.56	1.56

TABLE III. Representative experimental and calculated values of $1/\tau_\epsilon$, the tunneling probability from the excited KCl F center, versus ϵ , the applied field. It is assumed that m^* equals 0.5, and particular values of E and d are indicated.

$\epsilon \times 10^{-5}$ V/cm	$1/\tau_\epsilon$ sec $^{-1}$			Experimental
	$E=0.16$ eV $d=3.0$	$E=0.16$ eV $d=4.5$	$E=0.25$ eV $d=3.0$	
1.46	5.2×10^8	1.1×10^7	0.8	0.3×10^6
1.88	3.2×10^{10}	1.3×10^9	0.4×10^4	1.1×10^6

portance of measuring both τ and η_R . If one were to measure only one of these quantities he would have to assume a (probably constant) value for τ_R in order to determine τ_ϵ , whereas we can determine τ_ϵ directly.

Plots of $\ln[(1-\eta_R)1/\tau]$ versus $F(\kappa)$ indicate that $1/\tau_Q$ is negligible in this experiment; it is thus apparently a function only of temperature and is very small for such low temperatures.

In Table III are listed theoretical values of $1/\tau_\epsilon$ for two values of ϵ , obtained from Eq. (6) with the indicated values of m^* , E , and d . Also listed are the experimental values. Immediately one can see that there is a serious difficulty in obtaining agreement between theory and experiment. In the cases illustrated the theoretical values all change by at least 2 orders of magnitude, while the experimental value changes by only a factor of 4. It, in fact, turns out to be impossible to obtain agreement between the theory and the experimental results.

We shall comment more on these difficulties later, but let us point out what one *can* determine. First, it is clear that E is not as large as 0.25 eV, for even with a fairly small value of d (3.0) the tunneling probability is predicted to be very small from such a state. Second, if d is 4.5 (as is indicated from the Schottky experiment) E is probably between 0.16 and 0.18 eV. Such a value is reasonable since E should be somewhat larger than the thermal E_0 of the Schottky experiment. Since the polarization of the diffuse state arises in part because the ions "follow" the motion of the electron,⁷ it seems reasonable to expect that the ions will not remain at rest during the tunneling but will continue to follow the electron, and thus E should not be too much larger than E_0 .

It is interesting to compare our theoretical result with that of ES. If we insert typical values of $d=4.5$, $E=0.18$ eV $m^*=0.5$ into Eq. (6) and set $(1+\kappa)^{3/2}\mathbf{D}(\kappa)=1$, we obtain

$$1/\tau_\epsilon = 6.5 \times 10^{12-F(\kappa)E^{-1/2}d^{-1}(m^*)^{1/2}}.$$

The ES result is

$$1/\tau_\epsilon(\text{ES}) = 10^{15-F(\kappa)E^{-1/2}d^{-1}}.$$

The difference arises (1) because of our inclusion of m^* , and (2) because of our method of evaluating the denominator in Eq. (1). Their theory (with $d=2.3$, $E=0.159$ eV) would predict $1/\tau_\epsilon$ to be equal to 8×10^{11} sec $^{-1}$ for ϵ equal to 1.4×10^5 V/cm, whereas the observed value is $1/\tau_\epsilon = 0.25 \times 10^6$ sec $^{-1}$.

It is not particularly surprising that we have been successful in analyzing the Schottky data and not completely successful in analyzing the tunneling data. The Schottky effect depends only on the height of a potential barrier; it also occurs for relatively small applied fields. The tunneling effect, on the other hand, depends very critically on the shape of the barrier and the variation of that shape with the applied field. It also requires high fields (near the breakdown field) which may cause undesirable experimental effects to occur. A further point is that the WKB approximation, which has been used to derive the tunneling theory, is expected to be valid only for large quantum number n , whereas we have applied the theory to the $n=2$ level.

IV. SUMMARY AND CONCLUSION

We have used the luminescence technique developed by Swank and Brown to analyze the ionization of excited KCl F centers by applied electric fields. Measurements of the Schottky effect and their analysis provide quantitative agreement with the results of Fowler's theory of the relaxed excited F center. Measurements of the tunneling effect provide some qualitative agreement with the results of that theory.

There are several points which are worthy of further investigation. It would be interesting to study the decay characteristics of luminescence from states oriented in the z direction and compare these with the observations reported here. The experiments described here should be performed on other crystals, in particular those with small excited-state binding energy such as NaCl and CsBr.

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