THE RELAXED F CENTER

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Abstract. — The relaxed state of the *F* center is described in its relations and differences from the unrelaxed state. The most important experimental data referring to the emission phenomena is briefly reviewed ; particular attention is devoted to the radiative lifetime of the relaxed excited state ; nevertheless, photoconductivity data, electric field and stress effects are critically examined. Most of the comments are given in the framework of the « large orbit model ».

Recent data on emission energy, lifetime and thermal ionization energy, of the relaxed excited *F* center in NaF, KF, RbF are shown and an interesting dependence of $h\nu_{emiss}$ and τ_R on ε_∞ is discussed.

Résumé. — L'état relâché du centre *F* est décrit, en rappelant sa relation et différence avec celui pas relâché. Les plus importants résultats expérimentaux qui se réfèrent aux phénomènes d'émission sont brièvement discutés et l'on donne une attention particulière au temps de vie moyenne radiative de l'état excité et relâché ; cependant on va examiner critiquement les résultats de photoconductivité, des effets du champ électrique et des efforts appliqués. La plupart des interprétations est donné dans le cadre du modèle à large orbite.

On montrera des résultats nouveaux sur l'énergie d'émission, le temps de vie moyenne et l'énergie thermique d'ionisation du centre *F* excité et relâché dans NaF, KF, RbF et l'on discutera enfin une intéressante relation de $h\nu_{emiss}$ et de τ_R avec ε_∞.

Introduction. — The amount of knowledge on color centers increased so much in recent years that a limited argument as the theory and phaenomenology of the *F* center, the basic, most studied and better known color center is already an extremely wide subject for a single talk. Our present aim is more defined. We want to describe the « relaxed *F* center » and the phaenomena associated with it, discuss them in terms of the « large orbit » model, show some new data suggesting a new look on the beforementioned model. Further we limit our interest to the electronic problem, and set aside as much as possible the electron-lattice interactions.

To fulfil that task, in Section I we clarify what we mean for « relaxed *F* center » showing relations and differences which exist between the system we are dealing in absorption and emission experiments, respectively. In Section II we treat luminescence, photoconductivity and the effects on these properties due to electric field and uniaxial stress ; the theoretical background on these arguments will be briefly exposed. The quantities most thoroughly considered will be $h\nu_e$, the emission energy ; $\tau_R(2 p_r)$, or simpler τ_R, the radiative lifetime of the relaxed 2 *p* state, 2 p_r ; ΔE_i, the ionization energy of 2 p_r. In Section III recent data on $h\nu_e$, $\tau_R(2 p_r)$,

ΔE_i will be discussed and a new attitude on the large orbit model set forth.

I. The relaxed *F* center. — The *F* center is essentially an electron bound to the effective charge left behind by a missing halide ion ; the symmetry of its ground state electronic wave function is *s*-type ; the potential in which the electron moves is commonly described as a well (whose side is of the order of the lattice parameter and depth near to the Madelung energy) with a properly matched coulombian tail [1]. The first excited state is *p*-like and so are the others which can be reached with transitions allowed in the dipole approximation. The 1 *s* → 2 *p* transition gives origin to the *F* absorption band, the sum of 1 *s* → *np* transitions ($n = 3, 4, ..., \infty$) is responsible for the *K* band [2]. The *F* absorption band appears to be related to the well part of the potential since the energies of *F* band absorption peaks in alkali halides (only the f. c. c. ones) are inversely proportional to $d^{1,84}$ ($d =$ lattice parameter), a dependence very similar to that of the energy levels of a square well. This relation, usually called the Mollwo-Ivey law, suggests the idea that the charge distributions relative to the ground and excited wave function are concentrated inside the vacancy.

We have briefly sketched the system we sample in an absorption experiment, the unrelaxed F center : to be correct, in this case there should be inward lattice relaxation around the F center since the repulsive potential is changed, the F center electron, « softer » than the halide ion. Nevertheless, to describe this situation we will keep talking of unrelaxed F center, since this is the situation in which the F center spends most of its time.

We now imagine to send a quantum of light on the center : if the energy of the quantum corresponds to the difference in energy between the ground state and an excited state the quantum will be absorbed. As a consequence of such an event we might have, near zero degrees Kelvin, a pratically temperature independent (apart from temperature variation of electron mobility), fast photoconductivity if the transition is done to an excited but unbound state [4] or to the ionization continuum [5]. If the electron reaches a bound excited state the configuration of the nearest nuclei which is still the one in equilibrium with the ground state charge distribution will be in a stressed, non equilibrium position ; the electron in the excited electronic state will be in a highly excited vibrational state. Now the relaxation process takes place : in a time of the order of 10^{-12} sec. the nuclear configuration through lattice vibrations and loss of a considerable amount of energy (0,5 ∼ 1 eV) finds its equilibrium with the new charge distribution. Since in a p-like state the electronic charge is less concentrated inside the cavity and is less efficient in screening the effective charge at the center of the vacancy the nearest nuclei will move outwards. If the well gets wider the energy levels will be compressed and the distance E (ionization) $- E(2p)$ will become smaller, the classical orbit associated to the $2p$ state will have a greater radius and this will in turn decrease the charge inside the cavity and so the nuclei will relax further away until an equilibrium position will be reached.

This relaxation process will have different effects on the excited and on the ground state : the $2p_r$ state, will now find itself more and more in the coulombian part of the potential but the $1s$ relaxed state, $1s_r$, will still belong to an essentially well-type potential. In the model potential described at the beginning of this section, the dielectric constant to be associated to the coulombian part, the depth and the width of the well part will be different from the analogous values to be used for the unrelaxed F center and the difference will depend on the details of the relaxation.

If we are near absolute zero, the F center electron

will remain in the $2p_r$ state, ∼ 10^{-6}, 10^{-7} sec. and then decay with emission of a quantum of light of energy $E(2p_r) - E(1s_r)$; if we are at higher temperatures photoconductivity phaenomena have to be considered, but we will return on them later (non radiative decay processes common to higly concentrated F center systems will not be commented, here). When the electron will reach the $1s_r$ state, the lattice will be in equilibrium with the $2p_r$ charge distribution and, with loss of energy, (again ∼ 0,5, 1 eV) will accomodate to the new situation and the nearby ions will return in the position they occupied before the F center electron absorbed energy from the exciting quantum.

The relaxation process and its consequencies, as we have described them, represent the physical picture behind the « large orbit model ». To overcome the difficulty to explain the experimental values of τ_R for the F [6] and F_A center [7] it was necessary to allow that the $2p_r$ wave function becomes large (from here the name of the model) and the overlap integral with $1s_r$ smaller. W. B. Fowler [8] showed that he could obtain satisfactory agreement with the experimental data on τ_R, $h\nu_e$ and ΔE_i for NaCl with a variational calculation made in the spirit of the large orbit model. In our opinion the problem was not completely solved at that point for the way, somewhat arbitrary, in which the relaxation effects had to be introduced in the calculation but it was the most appealing proposal and the only that could give satisfactory explanation of experimental data. Other theories on the emission properties of the F center [9] have obtained non convincent agreement with experiments [10].

II. A. Einstein coefficients and radiative lifetime. — The first experimental data on the relaxed F center, F_r, to our knowledge, are the ones on the « high temperature photoconductivity » [11] (see (1)). Few years went by, before Van Doorn and coworkers detected the F center emission in some alkali halides [12], but great progress in the understanding of F_r was not achieved until the value of τ_R became known [6].

Before going into the details of the various experiments on F_r it will be convenient to recall the basic theory on the argument. Working on the Einstein relation between the induced absorption probability per unit energy density per unit time, times unit fre-

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(1) We must have clear the difference between the « low temperature photoconductivity » bound to the unrelaxed F center and the « high temperature photoconductivity » which is due to thermal ionization of the electrons which are in $2p$ state and is competitive with the radiation emission from the decay of the electron into the $1s_r$ state.

quency, B_{mk}, and the spontaneous emission probability per unit time, A_{km} :

$$A_{km} = \frac{1}{\tau_{km}} = \frac{8 \pi h v_{mk}^3}{c^3} B_{mk} \qquad (1)$$

where m refers to the ground and k to the excited state and v_{mk} is the absorption frequency, Fowler and Dexter [13] gave a relation that should be valid for any luminescent center in ionic solids. The expression given by these authors is :

$$\frac{f_{mk}}{\tau_{mk}^{-1}} = \left(\frac{\mathcal{E}_0}{\mathcal{E}_{eff}(E_{km})}\right)^2 \frac{\hbar^2 c^3 m^*}{2 e^2 n(E_{km})} \frac{E_{mk}}{E_{km}^3} \times$$

$$\times \frac{\Sigma_{\gamma\delta} \mid < r_{\gamma\delta} > \mid^2}{\Sigma_{\delta\gamma} \mid < r_{\delta\gamma} > \mid^2} \frac{(2 \mathfrak{I}_k + 1)}{(2 \mathfrak{I}_m + 1)} \qquad (2)$$

where f_{mk} is the oscillator strength of the absorption transition ; τ_{km}^{-1} has already been defined ; E_{mk} and E_{km}, the absorption and emission energies ; m^*, the electron effective mass ; $n(E_{km})$, the refractive index at the emission wavelength ; h, c and e have the usual meaning ; $\mathcal{E}_0$, the average field in the medium ; $\mathcal{E}_{eff}$, the effective field at the absorption or emission center ; $\mid < r_{\gamma\delta} > \mid^2$ and $\mid < r_{\delta\gamma} > \mid^2$, the dipole matrix elements expressed in terms of the electronic wave functions of the initial and final states γ, δ of the levels m and k ; the factor $(2 \mathfrak{I}_m + 1)$ and $(2 \mathfrak{I}_k + 1)$ arise from the degeneracy of the energy levels. If we imagine the center tightly bound we should use [13] $m^* = m$ and $\mathcal{E}_{eff}/\mathcal{E}_0 = 1 + \left(\frac{n^2 - 1}{3}\right)$; otherwise, m^* should have a proper, experimentally determined, value and $\mathcal{E}_{eff} \cong \mathcal{E}_0$: the effects of these corrections are rather weak. The most important terms of (2) are, obviously, the matrix elements of absorption and emission ; these might be equal one another (that would be the case of transitions involving inner, shielded electrons as in rare earth ions [13]) but, for the F center, the consequencies of relaxation make us believe that $\mid < r_{\gamma\delta} > \mid^2$ are bigger in absorption rather than in emission. Now, if one does not know the electronic wave function of the F center the only choice he has is to put $\Sigma_{\gamma\delta} \mid < r_{\gamma\delta} > \mid^2 = \Sigma_{\delta\gamma} \mid < r_{\delta\gamma} > \mid^2$; further, in the transition between ground and excited state both $^2S_{1/2} \rightarrow {}^2P_{1/2}$ and $^2S_{1/2} \rightarrow {}^2P_{3/2}$ are supposed to be involved. In the limits of such approximation, for KCl, τ_{km} (in our case $\tau_{2p,1s}$) $\cong 5 \times 10^{-8}$ sec.; simple sliderule calculations for alkali halides in which F center emission data exist, show that the theoretical lifetimes for these F centers are all in the 10^{-8} sec. range and similar within a factor of 3.

Let us go to the experiment ; to analyse the data we have to consider beside the luminescent emission also the thermal ionization or $2 p_r$; let us disregard for the moment other processes, sometime important, such as nonradiative decay and tunneling to the conduction band (the latter will be treated in the next paragraph). If we look to figure 1 we see that the
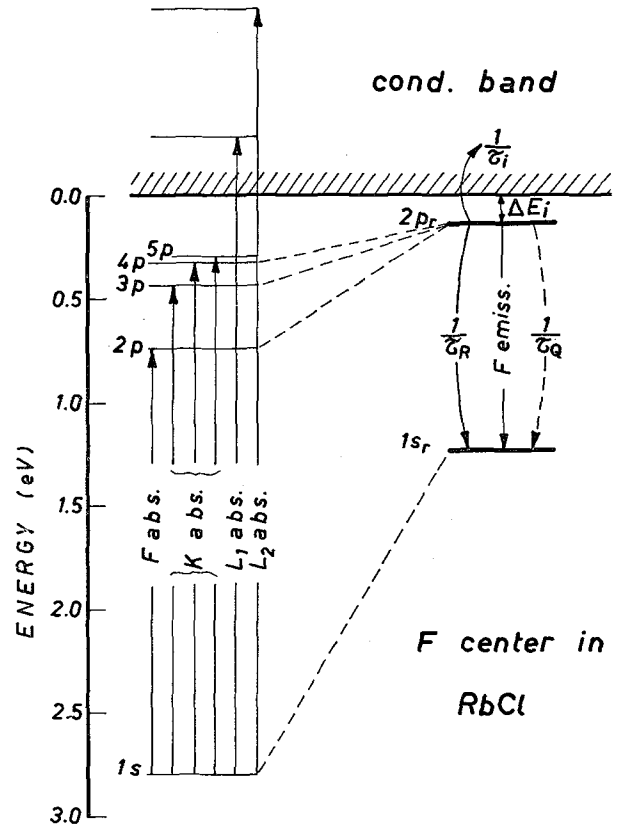

Fig. 1. — Energy level scheme for the unrelaxed and relaxed F center in RbCl.

radiation probability $1/\tau_{km}$ that we might call $1/\tau_{2p,1s}$ or $1/\tau_R$, plus the ionization probability (the high temperature photoconductivity) $1/\tau_i$ must give the inverse of lifetime of $2 p_r$, $1/\tau$:

$$\frac{1}{\tau} = \frac{1}{\tau_R} + \frac{1}{\tau_i} \qquad (3)$$

$1/\tau_i$ is usually written as $1/\tau_0$, an escape frequency, times a Boltzmann factor $e^{-\Delta E_i/kT}$. At the end :

$$\frac{1}{\tau} = \frac{1}{\tau_R} + \frac{1}{\tau_0} e^{-\Delta E_i/kT} . \qquad (4)$$

If, at a certain temperature, we shine light of properly chosen wavelength we will have n_0 electrons in the

excited state of the F center at $t = 0$ and they will decay with a law :

$$n(t) = n_0\, e^{-t/\tau} \qquad (5)$$

where τ is the one of eqn (4). Repeating the experiment at several temperatures and plotting the measured values of τ_i as a function of T we obtain graphs as those of figure 2. From easy manipulations of these data the value of $1/\tau_R$ and of ΔE_i is obtained.
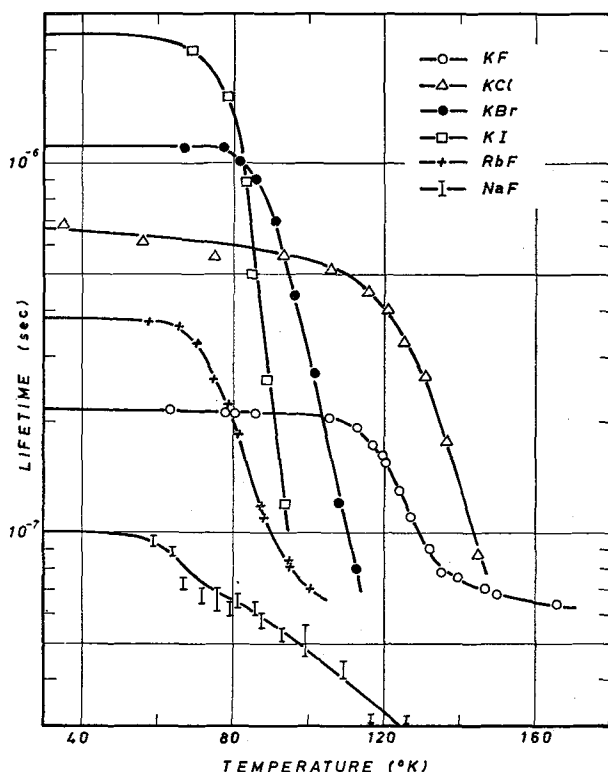

FIG. 2. — Lifetimes of fluorescence (NaF, KF, RbF, KCl) and photoconductivity (KBr and KJ). Data on KCl, KBr and KJ from reference [6] and R. K. Swank's Thesis. Data on NaF, KF, RbF are uncorrected for preamplifier rise time ; the correction is important below 10^{-7} sec.

$1/\tau$ can be measured both with luminescence [2] and photoconductivity experiments and the values of ΔE_i and $1/\tau_R$ obtained with the two different techniques turn out to be the same. Lifetime experiments are

[2] Practically the F centers are excited with filtered light from a spark gap and the luminescence pulse detected with an i. r. sensitive photomultiplier and via a cathode follower and preamplifier displayed on an oscilloscope screen and photographed. A different and very ingenious way to measure τ_R has been devised recently by FRÖHLICH (D.) and MAHR (H.), *Phys. Rev.*, 1966, **141**, 692.

particularly rich : if one studies integrated pulses, from the same picture of oscillographic display it is easy to get a number proportional to the total amount of emitted photons. If the rate of fluorescent emission is :

$$\frac{dn_R}{dt} = \frac{1}{\tau_R}\, n(t) = \frac{1}{\tau_R}\, n_0\, e^{-t/\tau} \qquad (6)$$

and

$$n_R = \frac{n_0}{\tau_R} \int_0^t e^{-t/\tau}\, dt = \frac{n_0\,\tau}{\tau_R}(1 - e^{-t/\tau}) \qquad (7)$$

for $t \to \infty$ (or, simply, for $t \geqslant \tau$) we have the possibility to determine the radiative quantum yield

$$\eta_R = n_R/n_0 \, ,$$

at a particular temperature. Photoconductivity quantum yield η_i, is analysed in the same way. Plotting :

$$\eta_R = \frac{n_R}{n_0} = \frac{1/\tau_R}{1/\tau} = \frac{\tau}{\tau_R} = \frac{1}{1 + \dfrac{\tau_R}{\tau_0}\, e^{-\Delta E_i/kT}} \qquad (8)$$

$$\eta_i = \frac{1/\tau_i}{1/\tau} = \frac{\tau}{\tau_i} = \frac{1}{1 + \dfrac{\tau_0}{\tau_R}\, e^{+\Delta E_i/kT}} \qquad (9)$$

as a function of temperature one can get ΔE_i.

This brief discussion on the analysis of experimental data should have shown that there are several possible controls to assure that the values of τ_R and ΔE_i are good ; of course, this is true within the limits of the model we assumed, from which retrapping and non radiative decay processes are excluded.

In table I, together with others, are reported Swank and Brown's data on KCl, KBr, KI and NaCl [6]. Since a comparison with calculations following the Einstein coefficient approach in the approximation $|<r_{\delta\gamma}>|^2 = |<r_{\gamma\delta}>|^2$ reveals a one order of magnitude mismatch these authors prospected two ways to explain the discrepancy : a) after absorption the electron may drop in an s-type lower excited state from which the downward transition to the $1\,s$ state is only partially allowed ; b) the electron remains in the same electronic level but this is drastically altered by the relaxation of the lattice, the excited state orbit becomes very large and the overlap integral with the ground state wave function is greatly reduced.

To decide among these suggestions a study was done on the F_A center [7], which is an F center where one of the six nearest neighbor alkali ions is substituted

by an alkali ion of lower atomic weight. If a 2 s level is important in determining the magnitude of τ_R, the different alkali ion, destroying the inversion symmetry, should have a relevant effect on the lifetime of $2 p_r$. In figure 3 is shown that this is not the case and the values of τ_R for F, F_A (Na), F_A (Li) in KBr are very similar ; ΔE_i does not change much, either. Certain F_A centers have « short » τ_R ($\sim 10^{-7}$ s and slightly below) and other anomalies too [14] but even if they
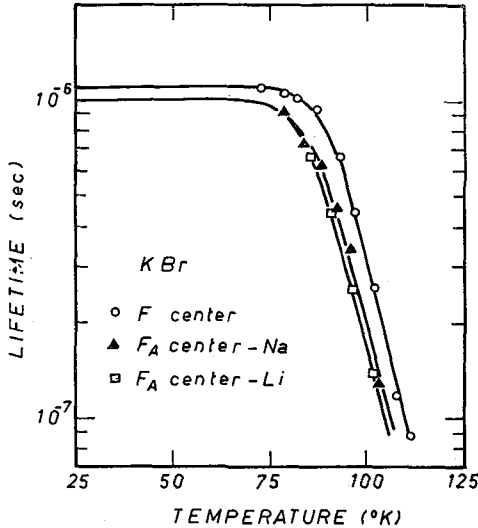

FIG. 3. — Lifetime of photoconductivity for F (from reference [6]), F_A (Na) and F_A (Li) centers in KBr.

are very interesting in their own, do not help much in understanding the problem of τ_R for the F center. From the F_A center τ_R and ΔE_i measurements it has been argued that the excited state wave function must be rather broad. If the ΔE_i is very little altered on going from F to F_A (Na) to F_A (Li) but some energy change is found in hv_{emiss}, the state most affected by the local ion substitution must be the ground one ; this fact matches the hypotesis that a broad $2 p$ wave function should not feel very much the change of one ion over many overlapped.

II. B. The large orbit model and related experiments. — The large orbit model as proposed by Swank and Brown and earlier by Mott and Gurney was then considered in detail by W. B. Fowler [8]. He used a variational approach with hydrogenic wave functions and determined the energy levels and oscillator strength for absorption. He then introduced relaxation (the large orbit hypotesis) allowing the mean radius of the $2 p$ wave function to increase and calculated the effective dielectric constant to be used

in the Hamiltonian for the relaxed F center. The same method used for absorption gave him the energy levels for emission and the values of the variational parameters of the wave functions from which he calculated the emission matrix elements : the ratio

$$| < r > |^2_{emiss} / | < r > |^2_{abs}$$

turned out be 0.13 in NaCl ; a good match was obtained with the experimental values of ΔE_i, hv_{emiss} and τ_R.

Some reason of dissatisfaction remained because with this method an « ad hoc » assumption for the $2 p_r$ wave function mean radius was necessary for each alkali halide ; further experimental evidence was sought to strengthen the large orbit assumption.

If $E(2 p_r)$ goes very near to the conduction band (~ 0.1 eV) and the orbit gets, for this reason, very large, the electron should sample an effective dielectric constant similar to the static dielectric constant, ε_s, and the potential for the $2 p_r$ level and higher ones until the ionization limit, largely coulombian. The data on ΔE_i were extended to other materials (NaF, RbCl, RbBr, CsBr) and the Rydberg formula :

$$\Delta E_i = E_\infty - E_{2p} = - \frac{e^4 m^*}{2 \hbar^2 \varepsilon^2_{eff}} \times$$

$$\times \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right) \cong - \frac{e^4 m^*}{8 \hbar^2 \varepsilon^2_s} \quad (10)$$

seemed to hold, in this limited energy interval, for the F center, too [15]. Few drawbacks were pointed out : the necessity to postulate m^* equal for all the alkali halides ; the, sometimes, ill determined values of ε_s ; the use of ΔE_i, a thermal depth, instead of an optical depth as the formula (10) would require. Further study was in order but this piece of evidence could not be refused.

An even stronger support to the large orbit model came from electric field effect studies on τ_R. Euwema and Smoluchowski [16] applied the Stark effect treatement for hydrogen to the F center and outlined two possible phaenomena : an high temperature Shottky effect and a low temperature tunneling effect. The Shottky effect consists in the lowering of the potential barrier which keeps the electron in the $2 p_r$ bound state. The extra photoconductivity or decrease in luminescent efficiency, due to Shottky effect, being aided by lattice vibrations, will be observed in the « high temperature » range. The tunneling effect, due to the quantum mechanical probability of crossing the barrier is temperature independent and relevant for higher values of electric field strength ; it can be

studied only at low temperatures, when the Shottky effect is insignificant. Experimental evidence of the existence of electric field effects already appeared in literature [17] but the explanation was not satisfactory : Spinolo and Fowler [18] extended the Euwema and Smoluchowski treatement and studied both the Shottky and tunneling effects.

As it has been said before the electric field, $\mathcal{E}$, decreases the potential barrier ΔE_i, which keeps the electron in the $2p_r$ state. The new ΔE_i, $\Delta E_i'$, for the $2p_x$ and $2p_y$ transverse states depends from $\mathcal{E}$ as :

$$\Delta E_i' = \Delta E_i - \left(\frac{2\,\mathcal{E}}{\varepsilon_{eff}}\right)^{\frac{1}{2}} \qquad (11)$$

where ΔE_i is the imperturbed ionization energy and ε_{eff} is an effective dielectric constant. The $2p_r$ lifetime expression will now be a bit more complex :

$$\frac{1}{\tau} = \frac{1}{\tau_R} + \frac{1}{\tau_0} e^{-\Delta E'/kT} + \frac{1}{\tau_{\mathcal{E}}} + \frac{1}{\tau_Q} \qquad (12)$$

with $1/\tau_{\mathcal{E}}$, the tunneling probability and $1/\tau_Q$, the probability for any other process that might lead to decay of the excited state. Fortunately the Shottky and tunneling effects can be studied separately because at low $\mathcal{E}$, $1/\tau_{\mathcal{E}}$ is very small and at low temperature $(1/\tau_0)\exp\left(\frac{-\Delta E_i'}{kT}\right)$ is negligible.
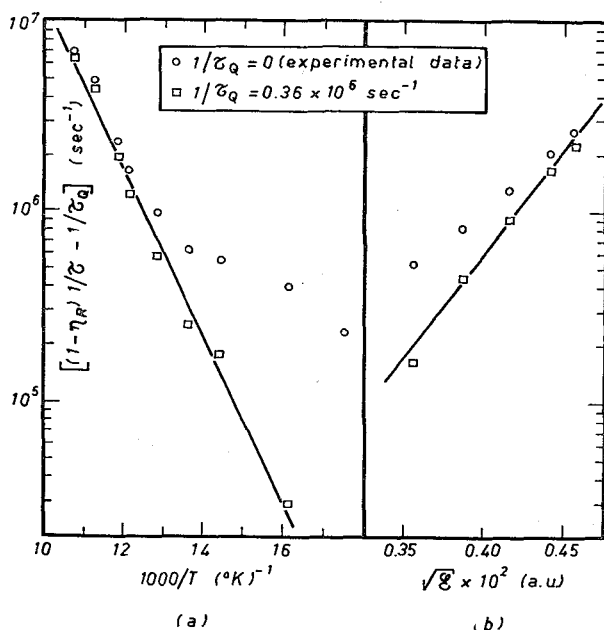
In figure 4 are shown the data on the Shottky effect

FIG. 4. — Plot of Shottky data for KCl F centers. For (a) $\mathcal{E}$ equals 7.7×10^4 Volt/cm, while for (b) T equals 77 °K.

taken both at fixed temperature and increasing field and viceversa. Analysing the data with the aid of eqn (12) and (11) it has been possible to obtain the value of ε_{eff} : in agreement with the large orbit hypotesis this turns out to be rather near to the value of ε_s. To analyse the data of figure 4 it has been necessary to consider the term $1/\tau_Q$: if we have negligible concentration effects (likely to aid non-radiative decay of $2p_r$) we do not know the process to which $1/\tau_Q$ refers but still this term is present both in τ_R and η_R data ; at present, hardly anything can be said on it but often, like in this case, it is necessary to take it into account on analysing the experimental data.

An interesting observation could be made also for the tunneling process. Since by definition

$$\eta_R(1/\tau) = 1/\tau_R$$

and we get for the same luminescent pulse both η and $1/\tau$ we might control that $1/\tau_R$ remains constant and temperature independent : this is in fact the case for relatively low field Shottky experiment, as shown in table I of [18]. For low temperature, tunneling experiments the product $\eta_R(1/\tau)$ does not remain constant with increasing electric field as we see from table II of reference [18] and this fact is the direct evidence of the change in wave functions, and therefore relative overlap and transition probability : one might claim that this is the first evidence of existence of Stark effect in emission. The analysis of tunneling data it has not been so easy for the limited range of electric field values in which it has been possible to study the effect : the results are in agreement with the large orbit theory, in the limits of their precision.

Interesting data of stress induced polarization of F center luminescence have also been published recently [19]. The normal F center luminescence, it is well known, is completely depolarized even if excited with polarized light ; the experiments reported by Hetrick and Compton show that it is possible to induce a partial wavelength, concentration and temperature indipendent polarization applying uniaxial stress to the crystal containing F centers. Their data have been succesfully interpreted in terms of emission from a p-like relaxed excited state which is very diffuse and largely unaffected by the stress, to an s-like ground state which is still mainly localized at the potential well and into which a small amount of d-like character is mixed by the stress. They evaluate an upper limit for the splitting of the excited p-state and point out that it is much smaller than the observed stress induced splitting of the $2p$ level in absorption. The large orbit model has been useful in the interpretation of this effect, too.

Studies of Park [20] on the optical absorption of the excited relaxed state which was populated with an high intensity ruby laser show an absorption in the infrared region attributed to the optical transition from $2\,p_r$ to the ionization continuum. The peak value of such an absorption should be the optical depth of the trap associated to $2\,p_r$ while the ΔE_i is the thermal depth.

III. **New data an** $h\nu_e$, ΔE_i **and** τ_R. — We might think now that we know a lot about F_r; we have a consistent picture which explains all the basic facts and also particular effects such as those due to electric field and uniaxial stress but still we must admit that the structure of our construction on the F_r is weak, since we need an « ad hoc » hypotesis to calculate τ_R, $h\nu_e$, ΔE_i in each alkali halide. Values of $h\nu_e$ were known for five alkali halides and from a plot of emission peak energy vs. the lattice parameter, to recall the Mollwo-Ivey law, nothing could be inferred [22].

At this point we thought that an extension of the data on the basic optical parameters was in order ; we have then measured ΔE_i, $h\nu_e$ [23] and τ_R [24] in other five alkali halides (NaF, KF, RbF, RbBr and RbJ) ; at the same time a detailed study on the vibrational problem basic parameters has been made. For all of these quantities the results came out to be of considerable interest.

Let us now consider the data on τ_R shown in figure 2 and collected in table I : we notice that there is a factor of ~ 20 between the τ_R of NaF, the shortest

and τ_R of KI, the longest. This factor is big ; no other parameter referred to the F center has so great a range : we must keep in mind, though, that $|\langle r_{\gamma\delta}\rangle|^2$ of eqn (2) are sensitive to small details of the wave functions much more than the energy levels. τ_R for NaF is of the same order of magnitude as τ_R for F_A (Li) in KCl and RbCl [14] ; these F_A centers have been said to be anomalous because they have an emission very shifted in energy respect to the absorption and a very short lifetime for the excited state ; a particular model implying deformation of the surrounding lattice has been introduced to explain these anomalies. At first sight the short lifetimes of the F center in alkali fluorides might seem anomalous too, but in our opinion, to understand these values of τ_R no particular model different from the one thought to be good for the other alkali halides should be postulated. The values of τ_R appear to be in a logical sequence of we plot them vs. ε_∞ as it is done in figure 5 : we see that the higher ε_∞ (smaller the attraction of the $2\,p_r$ electron from the effective charge at the center of the vacancy) the larger the $2\,p_r$ orbit respect to the one of $1\,s_r$ and the smaller the overlap integral. Further study is necessary to introduce these facts into the Einstein coefficient approach and calculate in a rigorous way τ_R but since now it appears that the shortest τ_R will remain the one of NaF and the longest (apart from caesium halides) should be the one for the F center in Li J.

Data on $h\nu_e$ have been plotted the same on figure 5 (read scale at the right side) and their dependance on $n^2 = \varepsilon_\infty$ should not be casual. As we see, $h\nu_e(\varepsilon_\infty)$ is

TABLE I

		NaF	NaCl	KF	KCl	KBr	KJ	RbF	RbCl	RbBr	RbJ
$h\nu_e$ (eV)	++	≠ 1.665	o 0.975	≠ 1,660	o 1.215	o 0,961	o 0.827	≠ 1.328	o 1.090	≠ 0.870	≠ 0.810
ΔE_i (eV)		Δ 0.055	+ 0.074	Δ 0.14	+ 0.150	+ 0.135	+ 0.11	Δ 0.075	⊕ 0.130	⊕ 0.11	Δ 0.082
$\tau_R(10^{-8}$ sec.)		Δ 10	+ 100	Δ 22	+ 57	+ 111	+ 222	Δ 36	⊕ 60	⊕ 60	Δ > 90
n^2		1.74	2.25	1.85	2,13	2,33	2,69	1.93	2,19	2,33	2,63

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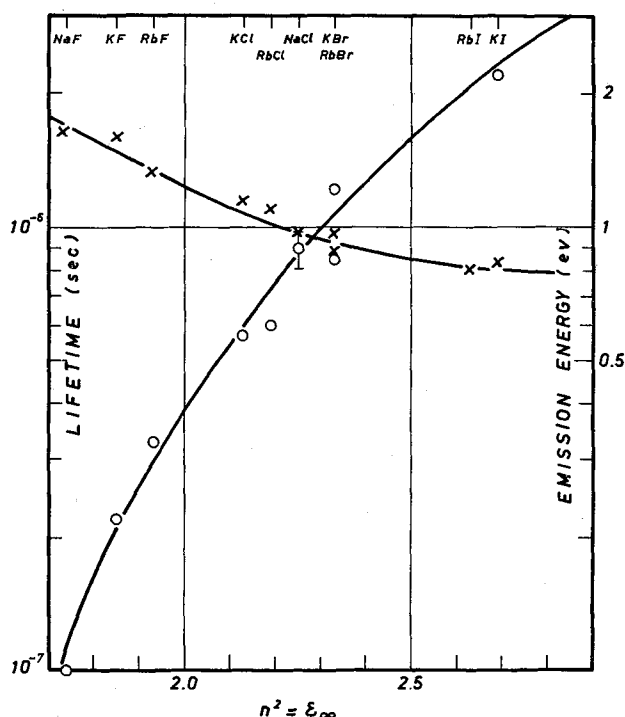≠ The labelled values are taken at liquid helium temperature.

FIG. 5. — Plot of τ_R (left scale) and $h\nu_e$ (right scale) vs. ε_∞ the continuous lines represent a best fit of experimental points.

much smoother than $\tau_R(\varepsilon_\infty)$ and has a negative slope : a qualitative explanation of the fact is parallel to the reasoning made on $\tau_R(\varepsilon_\infty)$. From these two laws we know in what time and wavelength range look for the τ_R and $h\nu_e$ of F centers in which these quantities are still unknown.

Since the beginning it was realized that the purely hydrogenic picture of ΔE_i on the grounds of eqn (10) it was on oversimplification and several objections were pointed out [15]. Fowler, later, observed [21] that, following the idea of a concentrated center the data of reference [15] were fitted as well. Since then, better values of ε_s have been published and several other ΔE_i values obtained [23, 24]. Both a large orbit [15] and concentrated orbit [21] plot turn out to give a poor fit of the experimental values ; the assumptions made on m^*, ε_{eff} and the identity of

$$\Delta E_i \equiv \Delta E_{thermal} \equiv \Delta E_{optical}$$

does not seem to be acceptable, now.

Even if the new experimental evidence is not against the large orbit model, certainly the empirical laws of figure 5 on τ_R and $h\nu_e$ suggest a new look on the line theory should pursue. The limit on the size of the $2 p_r$ orbit would be determined by the high frequency dielectric constant ; it seems no more believable that

ε_{eff} for $2 p_r$ is very near to ε_s and the ions follow the motion of the electron.

Further data on the electric field effects, near i. r. spectroscopy of F_r^*, detailed analysis of experiments on the vibrational problem in the frame of the theory now in development and a renewed theoretical effort on the electronic problem promise a deeper insight into the physics of the relaxed F center.

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