

line moments. Van Vleck has shown that at high temperatures it is sufficient to consider a truncated Hamiltonian which in our notation is given by

$$\mathcal{H} = g_{11}\mu_B H \sum_j S_{zj} + \sum_{k>j} (K_{11jk} - K_{1jk}) S_{zj} S_{zk} + \sum_{k>j} K_{1jk} \mathbf{S}_j \cdot \mathbf{S}_k.$$

The term in $\mathbf{S}_j \cdot \mathbf{S}_k$ does not contribute to the second moment at all, but it does contribute to the fourth and higher moments. In cases where the K_{1jk} are small, that is, when the interactions between the effective spins are mainly Ising, one expects to see a broad line which in simple cases may have structure corresponding to the different relative orientations of the nn. On the

other hand, if the K_{1jk} terms are comparable with, or larger than, the $K_{11jk} - K_{1jk}$ terms, then one observes an effective narrowing of the line due to the increased fourth moment. This is known as "exchange narrowing," although in the effective spin Hamiltonian approach the actual mechanism giving rise to the isotropic term may not be the exchange interactions at all.

From Table IV it may be seen that for both solutions 1 and 2 appreciable K_{1jk} terms are found for Ce^{3+} pairs in LaCl_3 , so that we would expect to see a single exchange-narrowed resonance line in the concentrated material. A prediction of the actual linewidth, however, requires a detailed theory for the line shape. Qualitatively, however, this is in fact what we observe experimentally.

Data and Speculations on the Electronic Problem for the Relaxed Excited F Center*

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The energies of absorption and emission peaks, the lifetime of the relaxed excited state, and the ionization energies of the relaxed excited state of the F center in NaF, KF, RbF, RbBr, and RbI have been studied down to the temperature of liquid He. The low-temperature shapes of the absorption and emission F bands, which have not been previously reported, are also shown. The data on these crystals represent limiting cases from several points of view and allow us to extend considerably the range of the parameters under study. As a consequence, the phenomenology now at our disposition is much more significant and allows us to propose a simple and realistic solution to the problem of the magnitude of τ_R . For the situation in which the F center is excited and relaxed, arguments in favor of the $2p$ level being lower in energy than the $2s$ are discussed.

I. INTRODUCTION

MANY efforts have been devoted in the last few decades to the understanding of the F -center absorption phenomenology, and in the following this problem will not be dealt with, since the basic facts are by now rather well understood.

The situation for the F -center emission has by no means reached a similar level of development. A great amount of fundamental data both on the electronic and on the electron-phonon interaction problem are still

lacking. Among the unanswered questions in this subject are the following.

(i) the theoretical prediction of the fraction of the absorbed energy given to the lattice and the fraction emitted;

(ii) the process through which the electron "forgets" the polarization due to the exciting electric field;

(iii) the mean time after which the emitted photon will emerge from the F center, restoring the electron to the ground state;

(iv) details concerning the number of channels through which the F center can be de-excited—even though the most obvious ones are known;

(v) information regarding the terms system after the lattice relaxes (in other words, the energy levels associated with the K band in absorption¹ do not reveal their

* Preliminary data have been presented at the Colloque sur les Centres Colorés, Saclay, 1967.

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¹ G. Spinolo and D. Y. Smith, Phys. Rev. **140**, A2117 (1965); D. Y. Smith and G. Spinolo, *ibid.* **140**, A2121 (1965).

presence in emission; other bound levels not showing up in absorption might play a relevant role.^{2,3}

Two topics of controversy may be added to the above list: the symmetry of the level from which the emission takes place, and the position in energy of the relaxed levels with respect to the locally perturbed conduction band.

A certain amount of theoretical and experimental activity (including our own) has been stimulated by the outstanding problems indicated above. Our approach in the investigation of the phenomenology of the *F*-center relaxed excited state has been the measurement and interpretation of the radiative lifetime τ_R and such associated quantities as $h\nu_e$, the emission energy, and ΔE , the ionization energy. A full description of the radiative lifetime phenomenology requires knowledge of the symmetry of the energy levels involved in the emission process and the amount of mixing, if any, of the initial and final states. The completeness of such a description implies the ability of predicting to a reasonable approximation the magnitude of τ_R , $h\nu_e$, and ΔE . Such data were available before the measurements herewith presented were undertaken do not fit a simple two-level model⁴ in the low-temperature region (in KCl below 80°K). In our opinion, neither are the few τ_R calculations made until now really satisfactory.

It was decided, therefore, to investigate the extent to which a broader range of measurements of such quantities as the emission energy $h\nu_e$, the relaxed excited state lifetime τ_R , and the relaxed excited state ionization energy ΔE might establish the function relating the variation of these parameters to the simpler fundamental physical parameters of the host lattice, such as the interionic distance or the dielectric constant. In the following a series of measurements of the quantities mentioned above is described. We then show that these measurements, unlike the limited data hitherto available, permit the derivation of important relationships which can predict these quantities for other cases.

In conclusion, in a way analogous to that by which the Mollwo-Ivey experimental law suggests a particle-in-a-box potential for the unrelaxed *F* center, we submit that the experimental relationships obtained are pertinent to the choice of the *F*-center potential for the relaxed state.

Further, we shall show that our experimental results yield interesting suggestions regarding the symmetry of the levels involved in the transition. The emission phenomenology in alkali fluorides unexpectedly reopens the problem of the physical meaning of ΔE , which had seemed reasonably settled.

Section II contains a brief description of our experimental apparatus and the basic information on the approximations we use to analyze the experimental data. Our results on $h\nu_e$, τ_R , and ΔE in NaF, KF, RbF, RbBr, and RbI, together with some other pertinent measurements, are given and commented upon in the same section.

In Sec. III we discuss $h\nu_e$, τ_R , and ΔE separately and outline our conclusions; when convenient some detail on the *F*-center absorption problem will be given.

The low-temperature behavior of τ_R , the emission quantum yield η_R , and the photoconductivity quantum yield η_i are discussed in the Appendix.

II. EXPERIMENTAL

A. Technique

The crystals we used were cleaved thin slabs (10×10×1 mm). The coloration in the fluorides was produced through x-ray irradiation at liquid-air temperature. Rubidium halides were colored both with x rays and additively with Rb metal.

Absorption measurements were performed with the sample in a stainless-steel liquid-helium cryostat, and the spectrophotometer was a Cary 14. Emission was measured with the sample in the same cryostat but with the aid of a Hilger quartz monochromator. A liquid-air-cooled 150 CVP Philips photomultiplier or a PbS Infracron detector, according to the spectral range of interest, were the detectors. The luminescence spectra have been corrected for prism dispersion and detector sensitivity. Luminescence τ_R and η_R were measured in the same cryostat and in an apparatus whose exciting source is a fast spark gap coupled to conveniently chosen glass filters. The detection was performed with a 150 CVP photomultiplier which feeds its signal through a preamplifier to a Tektronix 585 A oscilloscope. Photoconductivity lifetime data were taken with the same apparatus. In these measurements, however, the signal displayed on the oscilloscope screen does not come from a photomultiplier, but from the crystal itself, in which free charges, due to *F*-center ionization, drift in an applied dc field.⁴ The applied field was of the order of a few kV/cm. Photoconductivity data are not corrected for internal Shottky emission. A photoconductivity signal has to be produced by at least 10⁸ electrons to be efficiently analyzed.⁴

Pictures of the oscilloscope screen were taken with a common photographic camera loaded with Ilford HPS 135 film (ASA 800).

The temperature range in which we worked was 4.2–200°K. Measurements at different temperatures were made by letting the cryostat warm up spontaneously.

B. Data Analysis

It is perhaps useful at this point to outline the analysis of experimental data through which we derived τ_R and

² K. Park and W. L. Faust, Phys. Rev. Letters 17, 137 (1966).

³ W. B. Fowler, E. Calabrese, and D. Y. Smith, Solid State Commun. 5, 569 (1967).

⁴ R. K. Swank, Ph.D. thesis, University of Illinois, 1962 (unpublished); R. K. Swank and F. C. Brown, Phys. Rev. 130, 34 (1963).

ΔE (the way to obtain $h\nu_e$ is obvious). Let us begin by considering the possible channels through which the relaxed excited F center can decay after equilibrium has been reached.⁵ Let us write the following trial relation for $1/\tau$, the total inverse lifetime:

$$1/\tau = 1/\tau_R + (1/\tau)_{\text{high-temp. de-excit.}} + (1/\tau)_{\text{tunneling}} + (1/\tau)_{\text{low-temp. photocond.}}, \quad (1)$$

where the various terms will be described below.

(i) The radiative transition probability $1/\tau_R$, which contains the effect of the absorption and emission matrix elements, has been discussed at length by Fowler and Dexter.⁶

(ii) The term $(1/\tau)_{\text{high-temp. de-excit.}}$ involves the "high-temperature photoconductivity" and luminescence quenching phenomena. Through thermal activation by lattice vibrations, an electron in the relaxed excited state has a certain probability of going into the conduction band or, at least, out of that excited state. Typically such a probability is written $(1/\tau_0) \times \exp(-\Delta E/kT)$, where $1/\tau_0$ is a frequency of escape trials and ΔE is the activation energy for the jump.

(iii) The third term on the right describes tunneling. One possibility is that the electron of an excited F center tunnels to a neighboring F center, producing an F' center. This process is well known. We should not, however, exclude tunneling to impurity ions or to hole centers: The latter processes might be common in x-ray-colored crystals. There are reasons, though,⁷⁻¹² to think

⁵ G. Spinolo, J. Phys. (Paris)-C4 Suppl. au N. 8-9, 28, C4-23 (1967).

⁶ W. B. Fowler and D. L. Dexter, Phys. Rev. 128, 2154 (1962).

⁷ The tunneling phenomenon, strictly speaking, is dependent only on the thickness of the barrier and therefore on the concentration of the F centers. The fact that Miehlisch (Ref. 8) does not find a unit luminescence efficiency even at concentrations of the order of 10^{16} (F centers/cc) suggests to us, as to others (Ref. 9), the existence of inhomogeneities in F -center distribution and therefore that tunneling is always present. On this subject there is a recent, very interesting observation made with the single-photon delay measurement technique (Ref. 10): the F -center lifetime is constant even at concentrations of the order of 6×10^{17} (F centers/cc), where the radiative quantum yield is decreased to 30%; at the same time, the short-lived M luminescence appears, as has already been shown (Refs. 4 and 11). We can understand the effect considering that if over many excited F centers some are in proximity with other F centers and tunneling occurs with probability 1, the measured radiation quantum yield will decrease but the lifetime will not, since emission comes only from centers from which tunneling has a very low probability to take place. In such a situation, the concept of an average distance between two F centers, which causes quenching of luminescence (Refs. 8 and 12) through $F \rightarrow F'$ tunneling, would lose meaning. The tunneling situation we outlined above (no lifetime effects) is the one which controls the luminescence quenching at high concentration (otherwise we would have a shorter lifetime), but it still appears reasonable to have intermediate cases in which the tunneling is really one of the possible channels through which an excited F center might decay.

⁸ A. Miehlisch, Z. Physik 176, 168 (1963).

⁹ H. V. Watts and G. A. Noble, J. Chem. Phys. 40, 2051 (1964).

¹⁰ L. Bosi, C. Bussolati, S. Cova, and G. Spinolo, Boll. Soc. It. Fis. 55, 41 (1967); and (to be published).

¹¹ At concentrations $> 10^{17}$ (F centers/cc) a small concentration of M centers is unavoidably present. Since the M centers also are excited with F light, the combination of the two lifetimes (F and M) might give the impression in the single-pulse type of measurement that $\tau_R(F)$ becomes shorter with increasing concentration.

that tunneling involves mainly centers rather near each other, and is not competitive center by center with the other decay processes; it is therefore possible to drop this term in Eq. (1).

(iv) The term $(1/\tau)_{\text{low-temp. photocond.}}$ is now considered. It was observed in the early days of color-center research, and since then by several authors, that a photoconductivity excited in the F band persists at very low temperatures in colored alkali halides.¹³ This might be due to F' centers in so low a concentration as to be optically undetectable (these centers are photo-ionized at all temperatures) or to a process which occurs during or before relaxation. In either case, this term should not enter into the analysis of emission phenomena since it is not related to the relaxed excited state of the F center. We drop it from Eq. (1).

The relation (1) will therefore be used in the following form:

$$\frac{1}{\tau} = \frac{1}{\tau_R} + \frac{1}{\tau_0} \exp\left(-\frac{\Delta E}{kT}\right). \quad (2)$$

Making use of Eq. (2), we define the luminescence quantum yield

$$\eta_R = (1/\tau_R)/(1/\tau) \quad (3)$$

and the photoconductivity quantum yield

$$\eta_i = \frac{(1/\tau_0) \exp(-\Delta E/kT)}{1/\tau}. \quad (4)$$

In this approximation τ_R and η_R are temperature-independent in the region in which $\Delta E/kT$ is large. In reality this is not true; in the Appendix this point will be discussed.

To obtain ΔE one measures, at several temperatures, τ , η_R , or η_i , or all of them, for a consistency check. τ_R is usually obtained⁴ from a set of τ -versus- T data. In the Appendix we state as a conclusion of the discussion on the low-temperature behavior of τ_R , η_R , and η_i that the "best" value of τ_R is the one taken at the lowest possible temperature. In the next section the discussion of τ_R will be made using such values.

C. Measurements

Data on τ_R and ΔE

In the samples measured the F -center concentration never exceeded 1×10^{17} (F centers/cc). The data on the luminescence lifetime τ_R for the x-ray-colored alkali fluorides measured are shown in Fig. 1. Scattering in the data points referring to NaF may be observed. This is probably due to the low-level signal of the exciting

¹² W. D. Compton and M. N. Kabler, in Proceedings of the International Symposium on Color Centers, Urbana, Illinois, 1965, p. 31, (unpublished); G. Chiarotti and U. M. Grassano, Nuovo Cimento 46, 78 (1966).

¹³ G. Glaser, Nachr. Ges. Wiss. Göttingen 3, 31 (1937); F. Nakazawa and H. Kanzaki, J. Phys. Soc. Japan 22, 844 (1967).

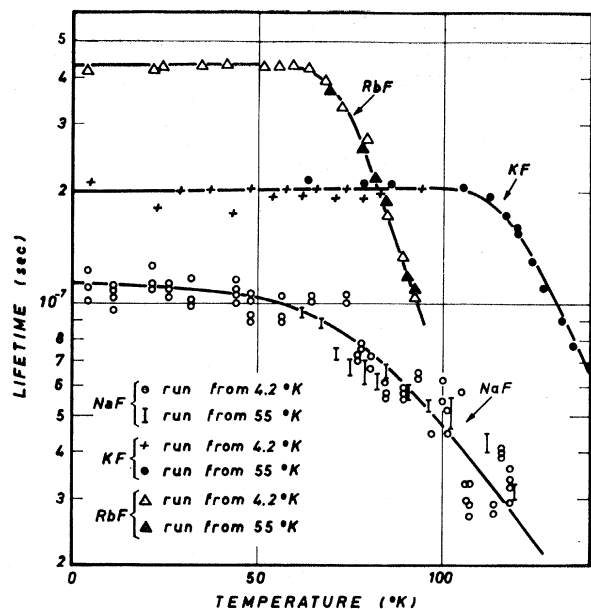


FIG. 1. Luminescence lifetime of the excited F center in NaF, KF, and RbF versus temperature.

source in the absorption region of the F center (the error in τ is $\sim 10\%$). Experimental points in KF and RbF are much better defined. It appears that in these materials τ does not exhibit the low-temperature behavior typical of KCl.⁴ From the data of Fig. 1, it may be observed that the fluorides have the shortest lifetimes among the halides of the same alkali. The NaF F center has the fastest emission of all the F centers we measured, and its τ_R is about two orders of magnitude shorter than that of the CsI F center, which is the longest.¹⁴

In Fig. 2 we show our luminescence-lifetime data for RbF and RbCl and our photoconductivity-lifetime data for RbBr and RbI. In the last two materials luminescence cannot be detected with a photomultiplier since it occurs at wavelengths longer than the extreme limits of photocathode sensitivity. At low temperatures the photoconductivity is so small that the point has probably not been reached at which τ is longest, and data analysis has become practically impossible because of the increasingly unfavorable signal-to-noise ratio. For the analysis undertaken in the next section we thought it wiser to use Frölich and Mahr's data for RbBr and RbI¹⁴; they are plotted along with our data in Fig. 2. From the data of Figs. 1 and 2 we obtained ΔE . The average values of ΔE obtained through η_R , η_i , or τ measurements are collected in Table I, together with the values of τ_R .

The fluorides we used were x-rayed. Some doubts might arise on the validity of comparing data taken on additively colored and x-ray-colored crystals. The impurities, in principle, might also have effects on the

F -center lifetime.¹⁵ To investigate this point we compared lifetimes at liquid-air temperature of additively colored KCl, x-rayed pure KCl, and KCl heavily doped with Co and Cu. The lifetimes turned out to be equal within our experimental error. Recently¹⁰ the statement regarding the equality of τ at 80°K on x-rayed and additively colored crystals has been confirmed with the experimental uncertainty reduced to values below 1%. A similar check has been repeated for photoconductivity experiments; additively colored and x-rayed KCl gave very similar results.

In the fluorides, however, the high-temperature photoconductivity was not revealed. The very weak and fast photoconductivity which was detected may be attributed to the low-temperature photoconductivity similar to that present in other crystals. This result suggests that the lack of high-temperature photoconductivity should not be attributed to an exceptionally low electron mobility, but it must be of a more intrinsic nature.

In these cases, where photoconductivity was not found although the luminescence showed an exponential temperature-dependent quenching, there remains the problem of interpreting the meaning of the ΔE we obtain from the analysis of the experimental emission data. In this respect, we note that the expression $(1/\tau_0) \times \exp(-\Delta E/kT)$ might be attributed to the probability of any thermally activated jumping process to a higher energy level. The process through which the excited F centers in alkali fluorides decay must therefore

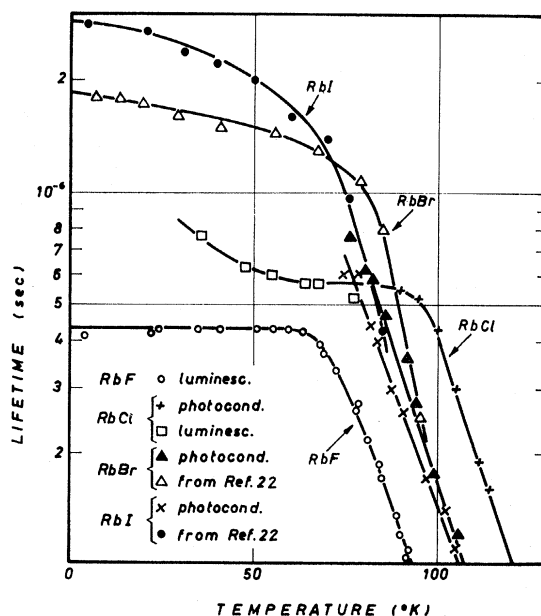


FIG. 2. Luminescence and photoconductivity lifetime of the excited F center in RbF, RbCl, RbBr, and RbI versus temperature.

¹⁵ This point was raised by F. Lüty during a private conversation with one of us (G. S.).

¹⁴ D. Frölich and H. Mahr, Phys. Rev. 141, 692 (1966).

TABLE I. Summary of the measured parameters for the *F* center.

	NaF	NaCl	KF	KCl	KBr	KI	RbF	RbCl	RbBr	RbI
$h\nu_e$ (eV) ^a	1.665 ^b	0.975 ^c	1.660 ^b	1.215 ^c	0.961 ^c	0.827 ^c	1.328 ^b	1.090 ^c	0.870 ^b	0.810 ^b
ΔE (eV)	0.055 ^d	0.074 ^e	0.14 ^d	0.150 ^e	0.135 ^e	0.11 ^e	0.075 ^d	0.130 ^f	0.11 ^f	0.082 ^g
τ_R (10 ⁻⁸ sec) ^a	11	100 ^h	20	80 ^e	111 ^e	330 ^h	42	75 ⁱ	180 ^h	280 ^h
n^2 ^j	1.74	2.25	1.85	2.13	2.33	2.69	1.93	2.19	2.33	2.63

^a The labeled values are taken at liquid-helium temperature.

^b Reference 17.

^c W. Gebhardt and H. Kühnert, Phys. Letters 11, 15 (1964).

^d Averages from emission quantum-yield and lifetime data.

^e Reference 4.

^f G. Spinolo, Phys. Rev. 137, A1495 (1965).

^g From emission quantum-yield data.

^h Reference 14.

ⁱ Measurement at 40°K.

^j Landolt-Börnstein Tables (Springer, Berlin, 1959), Vol. II, Part 6.

be nonradiative and nonphotoconductive for the temperature region where neither emission nor photoconductivity occurs.

Several measurements of the temperature dependence of the luminescence and photoconductivity quantum yield in the crystals in which photoconductivity has been found were performed by means of pulsed excitation. Luminescence quantum yields were also measured with steady excitation. All these measurements have been performed to obtain, by several different means, the values of ΔE collected in Table I.

One point that may be considered about these data is that in NaF, KF, and RbF (Fig. 1), τ does not exhibit a large variation in the low-temperature range, in contrast with what is seen in KCl and the other alkali halides. In the η_R -versus- T dependence, the alkali fluorides that we studied display in the low-temperature range a more pronounced decrease than the other alkali halides.¹⁶ A typical $[(1/\eta_R)-1]$ -versus- $1/T$ plot is shown in Fig. 3 for KF. The temperature dependence of η_R at low temperature introduces a slight ambiguity as to the choice of the temperature at which $\eta_R=1$; this fact, however, does not greatly perturb our evaluation of ΔE as is shown in (Fig. 3), which is obtained by extrapolation (see figure caption). In the Appendix a possible way of fitting low-temperature slopes to the experimental points is proposed.

For the alkali fluorides, measurements of quantum yield relative to KCl were also performed with the single-pulse technique. After correction for lamp emission, input filters, absorption of the specimen, emission, output filters, and photomultiplier response, it turned out that at 4.2°K $\eta(\text{KF})/\eta(\text{KCl})\approx 0.27$ and $\eta(\text{RbF})/\eta(\text{KCl})\approx 0.9$. The imprecision of photomultiplier sensitivity data in the wavelength region of lower sensitivity (where the KCl emission happens to be) might be partially responsible for the fact that the quantum-yield ratios are different from 1. A value of unity would, in fact, inspire confidence in the correctness of the comparison of lifetimes; however, all we can say is that the ratios are of the right orders of magnitude. In any case,

¹⁶ See the areas of curves 1-3 of Fig. 2 of F. Lüty and W. Gebhardt, Z. Physik 169, 475 (1962); see also Figs. 12 and 16 of R. K. Swank, Ph.D. thesis, University of Illinois, 1962 (unpublished).

we must remember that the data on concentration quenching¹⁰ indicate that while the yield may be small, the lifetime remains unperturbed.

Absorption and Emission Band Shapes

Since detailed data on $h\nu_e$ for KF, RbF, RbBr, and RbI and at low temperatures on $h\nu_a$ for NaF, KF, and RbF and $h\nu_e$ for NaF are not, to our knowledge, available in the literature, we present the results of our measurements¹⁷ herewith for future reference in Figs. 4-8. We notice in the emission curve of NaF evidence for a second band at ~ 1.3 eV, which might be due to some impurity excited in the *F* absorption band region. How-

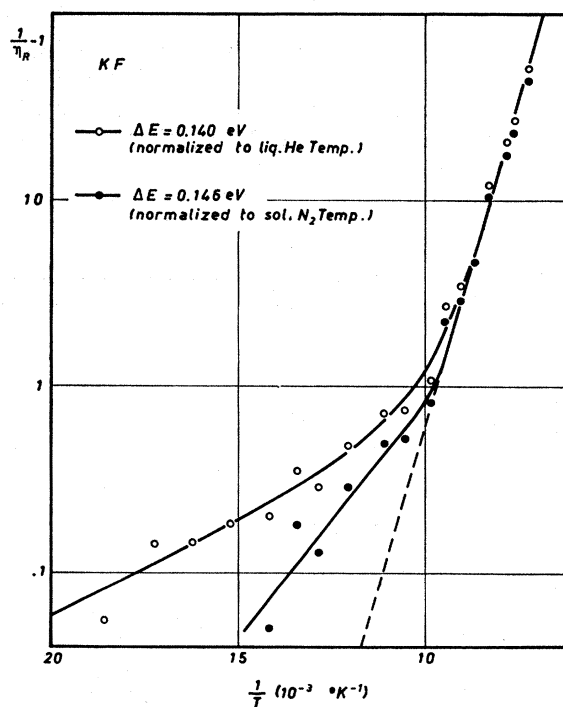


FIG. 3. $(1/\eta_R)-1$ versus $1/T$ for the excited *F* center in KF. The dashed straight line is an extrapolation of the best-fit line; its slope gives $\Delta E=0.146$ eV.

¹⁷ P. Podini and G. Spinolo, Solid State Commun. 4, 263 (1966).

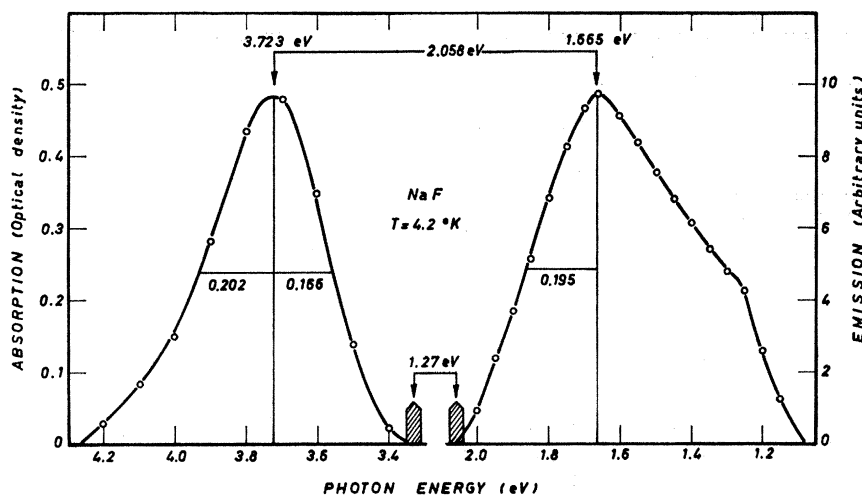


FIG. 4. Absorption and emission F bands in NaF at 4.2°K.

ever, since the low-energy semi-half-width is also relatively great in KF and RbF emission curves, this effect might be of a more intrinsic nature, and further study on this problem might prove to be of considerable interest.

K bands were not observed in any of the fluoride F -center absorptions. The tail of the absorption curve of RbF at low energies was not studied in detail, because of the high hygroscopicity of RbF, but we are inclined to attribute it to an F' band.

In RbI the spin-orbit splitting of the $2p$ level reveals itself not only through a large asymmetry of the absorption band but also through fine structure in the absorption curve of the same type for the cesium halides. This represents a confirmation of other authors' data.¹⁸ In these figures we also give the low- and high-energy semi-half-width, the Stokes shift, and the estimated shift

between the position of the absorption and emission zero-phonon lines, if these lines were detectable (the hatched areas in Figs. 4-8 refer to the zero-phonon regions). This quantity appears to be of some interest since it has been recently suggested that it represents¹⁹ the strain energy stored in the lattice during relaxation. It has been found that, for F centers in which the Jahn-Teller effect and the spin-orbit splitting are unimportant, a linear relation holds between this strain-energy term and $1/\epsilon = 1/\epsilon_0 - 1/\epsilon_\infty$, the inverse of the effective dielectric constant for lattice polarizability.

III. DISCUSSION OF EXPERIMENTAL DATA

A. Ionization Energy ΔE

Let us first consider the situation of the higher excited states in absorption. Photoconductivity experi-

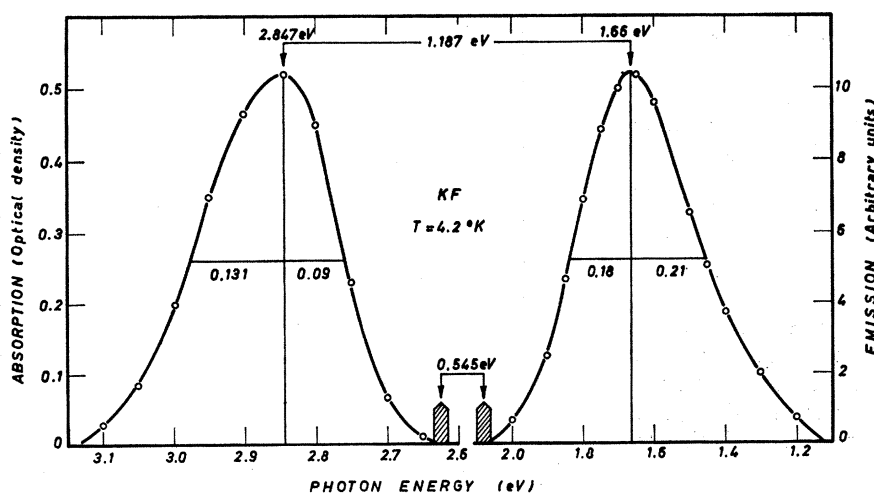


FIG. 5. Absorption and emission F bands in KF at 4.2°K. Notice the change of energy scale for emission band.

¹⁸ F. C. Brown, Notes of the NATO Summer School—Ghent, 1966 (unpublished).

¹⁹ E. Mulazzi, G. F. Nardelli, and N. Terzi, Phys. Rev. **172**, 847 (1968).

FIG. 6. Absorption and emission F bands in RbF at 4.2°K.

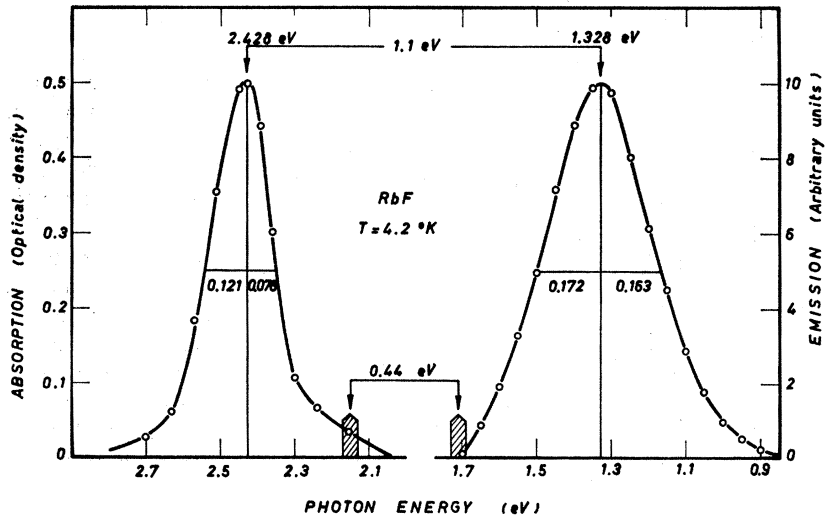


FIG. 7. Absorption and emission F bands in RbBr at 4.2°K.

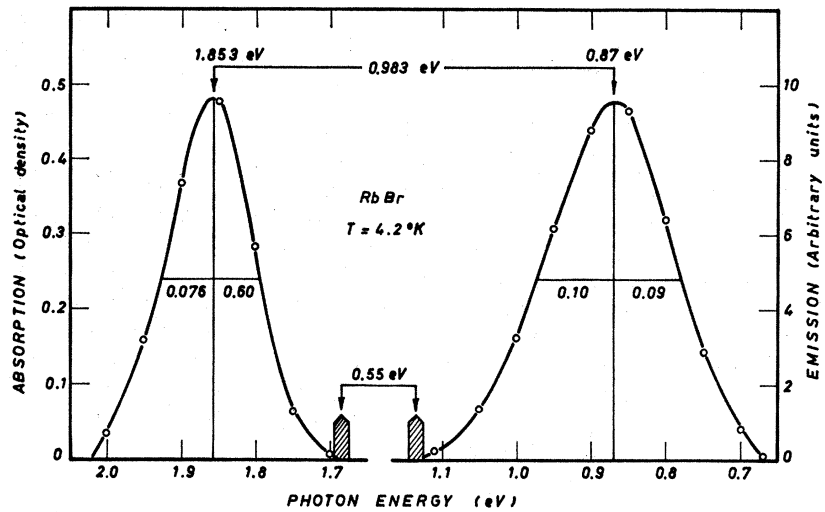
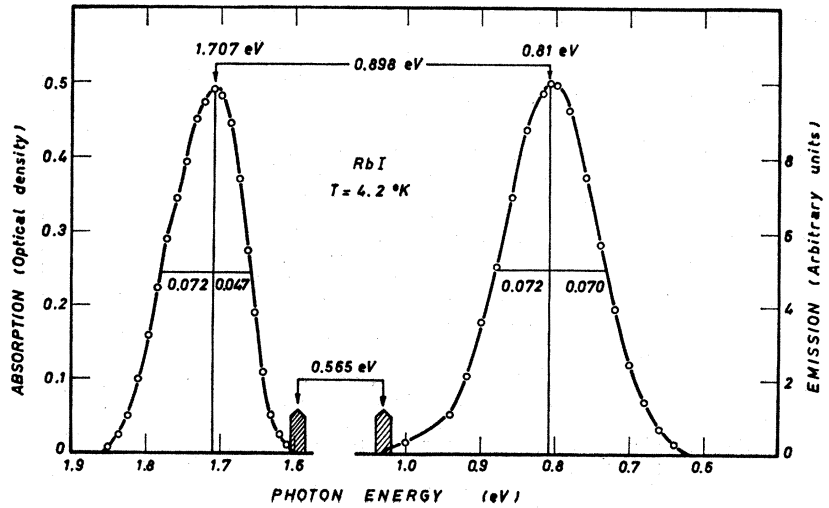


FIG. 8. Absorption and emission F bands in RbI at 4.2°K.



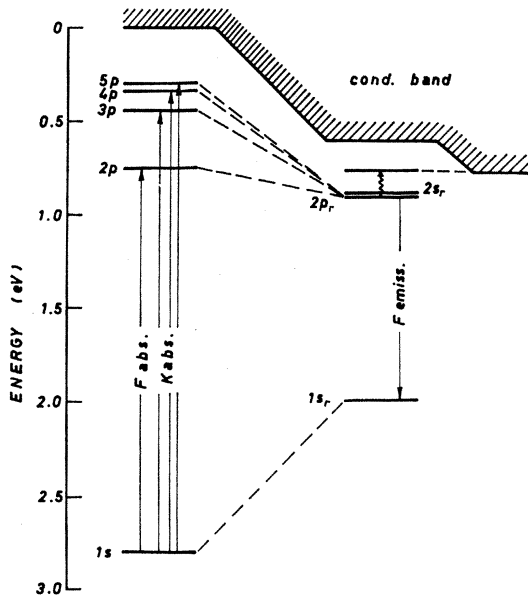


Fig. 9. Absorption and emission energy level scheme for the F center in RbCl.

ments indicate, under certain assumptions, that the difference in energy between the F -band peak related to the $2p$ level and the ionization continuum is ~ 0.6 eV in typical cases.¹ This interpretation is based on the hypothesis that the bottom of the conduction band and the ionization threshold for the F center coincide.

If the F center is now excited, the surrounding lattice will relax and the levels will be pulled together; $h\nu_e$ then turns out to be approximately half of $h\nu_a$. In a dielectric-continuum approximation a similar factor should be applied to the "optical" distance from $2p$ to the ionization continuum²⁰⁻²³ (0.6 eV is replaced by ~ 0.3 eV), if we want to introduce the hypothesis that after relaxation the bottom of the conduction band and ionization limit of the F center coincide.²⁴ Experimentally (when photoconductivity exists) the ΔE we measure is a "thermal" distance between the relaxed excited state and the bottom of the conduction band. We see from Table I that thermal values are about a factor of 2 smaller than the theoretically estimated optical ones.

²⁰ We should not expect to find that an electron excited with a quantum corresponding to the $1s \rightarrow 3p$ transition, for example, remains in the $3p_r$ relaxed state. Even if the lifetime of $3p_r$ is of the same order as atomic lifetimes (Ref. 21) there is plenty of time for lattice vibrations to make it decay into the lower $2p_r$. It should be possible to elucidate the role of the d states, however, by means of suitable experiments, since the oscillator strength from $2p$ to $3d$ has been calculated as 0.37 (Ref. 3). The $2s$ state might have an important effect on the emission process as well. Recently, in fact, interesting proposals on τ_R implying a lower $2s$ state have been made (Refs. 22 and 23).

²¹ W. S. Bickel and A. S. Goodman, Phys. Rev. **148**, 1 (1966).

²² M. Tomura, T. Kitada, and S. Honda, J. Phys. Soc. Japan **23**, 454 (1967).

²³ L. D. Bogan, Ph.D. thesis, Material Science Center, Cornell University, 1968 (unpublished).

²⁴ To the authors' knowledge this point has never been discussed from a rigorous theoretical standpoint.

In the alkali fluorides, since there is no photoconductivity, ΔE cannot have the same physical meaning. For the fluorides we can think of a nonradiative de-excitation process, competitive with luminescence, with an activation energy lower than that necessary to jump to the conduction band. This process should also explain Podini's²⁵ photostimulated thermoluminescence data. The traps which hold the electrons until they are thermally excited to give the glow peaks must be filled through a tunneling process from the relaxed excited state, or else are extremely long-lived higher excited levels of the same center; otherwise we would see photoconductivity.

If we take another attitude and prefer to have a single picture for all the F centers, we might postulate the intervention of a higher excited level, $3d$ for example, in all the cases and simply think that it is usually degenerate with some d -character point of the conduction band. An exception is the alkali fluorides, in which this point might be much higher in energy. In Fig. 9 we give an illustration of our proposal which, we repeat, represents only a first approach to a unifying solution of the problem.

B. Emission Energy $h\nu_e$

Let us now examine the situation for the peak of the F absorption band. Two empirical laws^{26,27} have been proposed to relate the magnitude of the absorbed quantum to the parameters of the host crystal. The Mollwo-Ivey law, based on the hypothesis that the F -center electron behaves in absorption as a particle in a box with dimensions proportional to the lattice parameter, has recently received good theoretical support.²⁸ Until the present time little attention has been given to Levy's relationship

$$h\nu_a = 3e^2/8R_{\text{cst}}\epsilon_{\infty}, \quad (5)$$

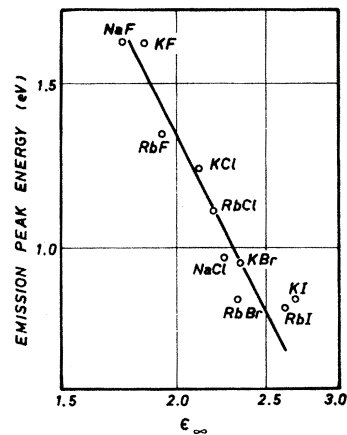


Fig. 10. Low-temperature values of emission peak energy versus ϵ_{∞} .

²⁵ P. Podini, Phys. Rev. **141**, 572 (1966).

²⁶ M. Levy, Nature **177**, 241 (1956).

²⁷ H. F. Ivey, Phys. Rev. **72**, 341 (1947).

²⁸ R. F. Wood, J. Phys. Chem. Solids **26**, 615 (1965).

where R_{cat} is the cation radius. This relation contains elements of the continuum hydrogenic approximation, since it is of the Rydberg law form for a $1s-2p$ transition. However, instead of using $\epsilon_{\infty}\hbar^2/e^2m^*$ as the radius of the $1s$ state and allowing it to change with the high-frequency dielectric constant of the medium, Levy chose the same radius for all crystals with the same halide ion. In fact, the inward relaxation due to the change of the repulsive potential of the object inside the six alkali ions should produce an identical r_{1s} . The reason why Levy chose $r_{1s}=R_{\text{cat}}$ is not clear to us. To conclude, we must say that both the Mollwo-Ivey and Levy laws have comparable success in classifying absorption peak measured energies.

We now consider $h\nu_e$ in the various alkali halides. For the present discussion definition of the symmetry of the emission starting level is not essential. A suggestion has already appeared on the dependence of $h\nu_e$ on the high-frequency dielectric constant.^{5,29} In Fig. 10 we see that the law $E_{\text{emiss.}}\epsilon_{\infty}^2=5.25$ is reasonably verified in the approximation $m^*=0.5$ for all the alkali halides.

If we consider the Rydberg law

$$(E_{2p}-E_{1s})=-\frac{e^4m^*}{2\hbar^2\epsilon_{\infty}^2}\left(\frac{1}{2^2}-\frac{1}{1^2}\right), \quad (6)$$

$$E_{\text{emiss.}}\epsilon_{\infty}^2=10.15m^*, \quad (6')$$

we notice that not only the functional dependence but also the value of the constant appears to be verified. Following Levy's proposal for the *F*-center absorption problem as a working hypothesis for the relaxed *F* center, a Coulomb potential was used. The only change we introduced is that for the relaxed *F* center the electron orbit radius also depends on ϵ , as it also occurs for electrons bound to impurities in semiconductors.

We believe that a theoretical discussion on the limits of validity of such a proposal would be extremely useful, and would also throw some light on the ΔE problem.

C. Excited-State Radiative Lifetime τ_R

In the spirit of Eq. (6) and Fig. 10 we plotted the values of τ_R we obtained, together with those measured by other authors^{4,14} (liquid-helium temperature data), against ϵ_{∞} in Fig. 11. From this plot we see that

$$\tau_R=K\epsilon_{\infty}^{-7.5}, \quad (7)$$

where K is a constant.

We tried, unsuccessfully, to derive such a dependence on ϵ_{∞} from the expression for τ_R in Ref. 6. This was done assuming that the absorption was between the $1s$ and the $2p$ levels and the emission between the $2p_r$ and the $1s_r$ levels, where the subscript r indicates the relaxed

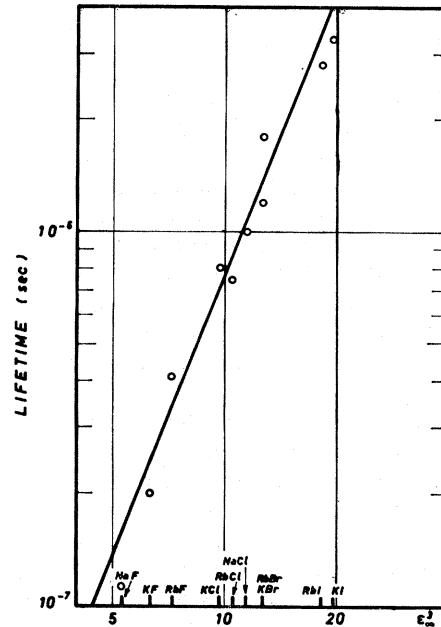


FIG. 11. Low-temperature values of τ_R versus ϵ_{∞} .

state. Absorption matrix elements were held constant as a function of ϵ_{∞} , since the absorption oscillator strength changes little from one alkali halide to another. The emission matrix elements were calculated assuming a hydrogen atom in a dielectric continuum.

We proceed now without taking a position on the form of the potential, and leave the discussion of the potential to a further stage of development of the problem. We just observe that, on the grounds of Figs. 10 and 11, ϵ_{∞} seems to play a key role in determining the magnitude of $h\nu_e$ and τ_R . Specifically, the $2p$ and $1s$ levels become closer together as ϵ_{∞} increases. The $2p$ and $2s$ levels behave similarly. The latter levels, since they are rather close together³⁰ even in absorption, will very likely be mixed by lattice vibrations of the appropriate symmetry after relaxation. NaF has the lowest ϵ_{∞} , the largest distance $2p_r-2s_r$, and, if $2p_r$ is lower, an almost purely $2p_r \rightarrow 1s_r$ allowed transition and the shortest lifetime. In summary we think that size effects, in the same way as suggested in the "large-orbit theory"³¹ are relevant to bring τ_R from, say, the 10^{-8} -sec to the 10^{-7} -sec region. We also attach the greatest importance to wave-function mixing and the energy distance between $2p_r$ and $2s_r$ which, on the grounds of Eq. (7) and data of Fig. 11, appear to be controlled by ϵ_{∞} . If the $2s_r$ is lower than $2p_r$ state, then it would be, in general, the emission starting level. Then the smaller ϵ_{∞} is, the greater the separation $2p_r-2s_r$ becomes, and hence the lower the mixing and the longer the lifetime. From our data we learn that τ_R gets shorter as ϵ_{∞} becomes smaller.

²⁹ L. Bosi, P. Podini, and G. Spinolo, *Boll. Soc. It. Fis.* **55**, 42 (1967); also, along the same line, see R. L. Gilbert, *Phys. Letters* **25a**, 382 (1967); R. L. Gilbert, Oak Ridge National Laboratory Internal Report No. ORNL-TM-2054 (unpublished).

³⁰ G. Chiarotti, U. M. Grassano, and R. Rosei, *Phys. Rev. Letters* **17**, 1043 (1966).

³¹ W. B. Fowler, *Phys. Rev.* **135**, A1725 (1964).

Experimental data, therefore, seem to require $2p_r$ (lower than $2s_r$) to be the emission starting level. This solution to the problem of the magnitude of τ_R as a function of the host crystal macroscopic parameters appears to be both simple and realistic.

Our model is essentially different from the one due to Tomura and co-workers²² in the order of the $2p_r$ and $2s_r$ levels. On the grounds of the temperature dependence of electric-field-induced emission polarization, Bogan²³ gives good evidence in favor of the $2s_r$ (lower than the $2p_r$) level being the emission starting level; a theoretical suggestion of a crossing of the $2s_r$ and $2p_r$ states has also been reported.³ Far from disregarding these facts, a further discussion is warranted.

From Fig. 2, we see that the slope of τ versus T in the low-temperature region is negligible in RbF and rather relevant in RbI. If temperature-activated lattice vibrations only increase mixing of the $2p_r$ with $2s_r$ (apart from the cases like RbF, KF, and NaF, in which mixing should not be important for the reason that ϵ_∞ is low, and therefore $2p_r$ is better separated from $2s_r$) and the lifetime decreases, we would be inclined to think that in the emission starting level the $2p$ percentage increases with temperature and so at the lowest temperature the most important contribution should come from a $2s_r$ level lower than the $2p_r$. If the lattice vibrations increase the splitting $2s_r - 2p_r$, the shortening of lifetime seems to suggest that the $2p_r$ level is lower.

We know that certain lattice vibrations mix electronic wave functions but others shift the levels and others do not have appreciable effects. According to the frequency of the vibrations with such characteristics, a certain temperature will succeed in exciting few or many phonons, and so we believe that it is important to have a detailed study of the influence of lattice vibrations on the mixing and splitting of $2p_r$ and $2s_r$ levels. From such a study one would hope to understand not only the temperature dependence of τ in the low-temperature region, but also to deduce the order of $2s_r$ and $2p_r$ states; in other words, one should have a final breakthrough on the τ_R problem.

On the experimental side we believe that an extremely detailed measurement of the temperature dependence of τ in the 4.2–70°K range with the single photon delay measurement technique,¹⁰ now in progress, will be the adequate counterpart of the theoretical study that we suggest.

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We are pleased to thank W. B. Fowler for useful correspondence. Interesting discussions have been held with F. Lüty, and our colleagues E. Mulazzi, G. F. Nardelli, and N. Terzi. We are grateful to Professor D. B. Fitchen and Dr. R. L. Gilbert for communicating to us the status of their research on the same subject. Finally, the help of Dr. C. J. Bland in correcting the language has been invaluable.

APPENDIX: LOW-TEMPERATURE BEHAVIOR OF τ_R , η_R , AND η_i

If Eq. (2) applies to our problem, the behavior of τ versus T should vary as the dashed curve in Fig. 12, and η_R should vary as the dashed curve in Fig. 13.

Under the same hypothesis, η_i should behave as the dashed curve in Fig. 14. The use of Eq. (2) permits the derivation of expressions for the variation of τ_R , η_R , and η_i with T . These relationships are plotted in the dashed curves of Figs. 12–14.

Experimental data on the photoconductivity yield in KCl⁴ are shown by the black circles in Fig. 14. These have been corrected for electron mobility³² and normalized to unity; the corrected data are shown by the open circles. It may be observed that the resultant yield of the low-temperature photoconductivity, described in Sec. II B, turns out to be lower than 10^{-4} . This low value implies that this phenomenon may be neglected in the study of τ , even though it is qualitatively interesting and rather puzzling.

If low-temperature photoconductivity may therefore be neglected and we further do not take $(1/\tau)_{\text{tunneling}}$ into consideration for the time being, then both τ and η_R should not depend on temperature below about 85°K (in KCl, for example). Now, this behavior is not supported by experimental evidence either in the case of η_R ¹⁶ or in the case of τ . The latter, in fact, varies by about 15% in the case of KCl in the temperature range 80–4.2°K.⁴ Some authors^{22,23} explain this temperature variation as due to the fact that a phonon-violated forbidden transition occurs. We might add that the varia-

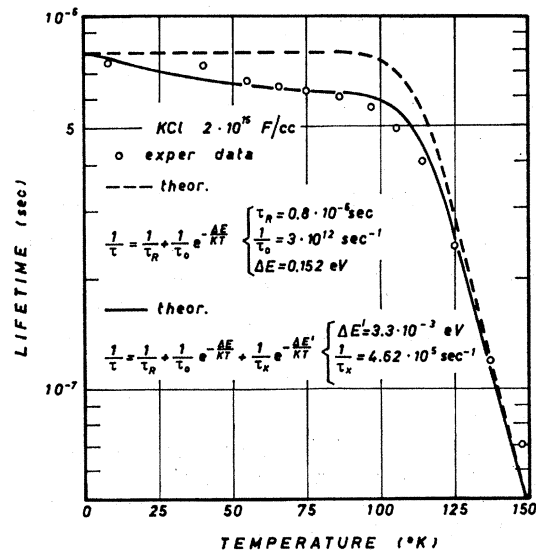


FIG. 12. Luminescence lifetime of the excited F center in KCl versus temperature. Experimental data (open circles) are compared with two kinds of theoretical plots.

³² F. C. Brown and N. Inchauspé, Phys. Rev. **121**, 1303 (1961).

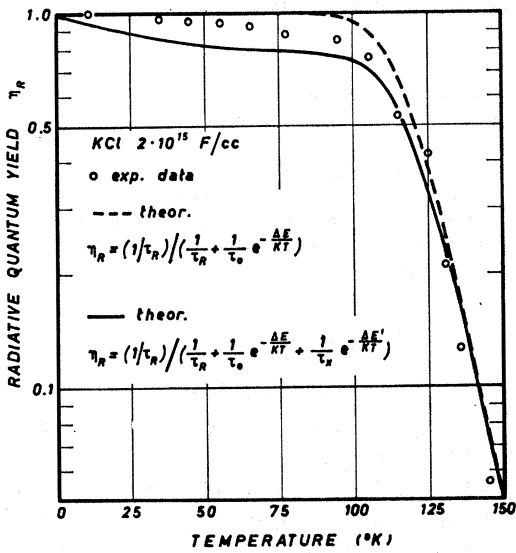


FIG. 13. Luminescence quantum yield of the excited F center in KCl versus temperature. Experimental data (open circles) are compared with two kinds of theoretical plots, in which $1/\tau_x$ and $\Delta E'$ values are the same as in Fig. 1.

tion of τ versus T in this low-temperature range will be greater as the Debye temperature of the crystal is lower. In Fig. 2 experimental data on the Rb halides seem to confirm our statement. An alternative way to view the problem would be to assume a level which is $\Delta E'$ higher in energy than the one from which emission takes place and to use an analytical expression such as $(1/\tau_x) \times \exp(-\Delta E'/kT)$ for the probability of jumping to such a level. Using this model, a good match with the experimental data for KCl is obtained with the values $1/\tau_x = 4.62 \times 10^5 \text{ sec}^{-1}$ and $\Delta E' = 3.3 \times 10^{-3} \text{ eV}$. This is shown by the continuous line in Fig. 12. η_R data are not satisfied in the same way, as seen in the continuous line of Fig. 13. The continuous line of Fig. 14 shows beyond doubt that the process we proposed as an hypothesis does not cause photoconductivity. We can further state that the process giving low-temperature variations on τ and η_R cannot be a radiative one, since, following the emission decay over about four orders of magnitude in

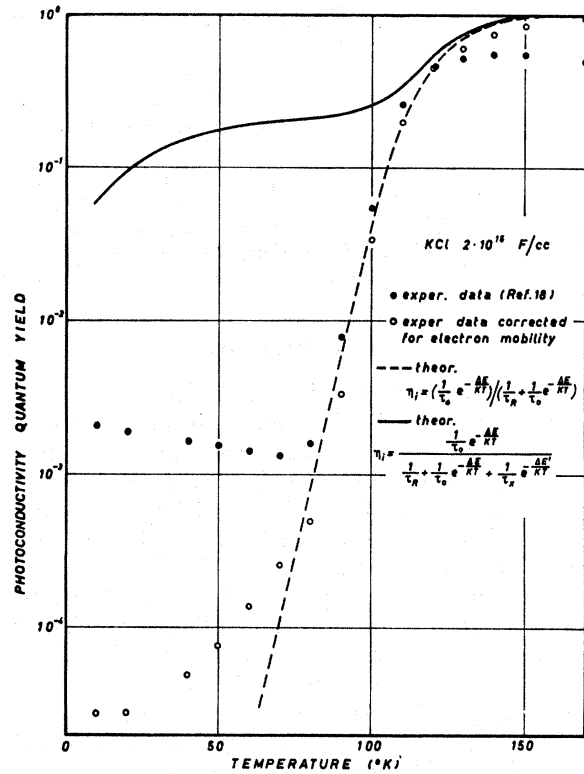


FIG. 14. Photoconductivity quantum yield of the excited F center in KCl versus temperature. Experimental data corrected for electron mobility (open circles) are compared with two kinds of theoretical plots, in which $1/\tau_x$ and $\Delta E'$ values are the same as in Fig. 1.

intensity with the single photon delay measurement technique,¹⁰ at 77°K, only one slope has been found.

It seems reasonable to conclude that the best values of τ_R and values of η_R nearest to unity have to be obtained from the lowest-temperature data on such parameters. In cases where luminescence experiments cannot be performed for lack of sensitive detectors, we think that the best values of τ_R are obtained with the technique of Frölich and Mahr¹⁴ rather than with photoconductivity measurements, since in this case the detection of τ in the small low-temperature signals is rather difficult.