tures being due to dislocation scattering. Moss's values for the scattering strength of dislocations in CaF_2 [13] can be used to estimate the dislocation density necessary to produce the observed conductivity. The value needed is 10^7 cm^{-2}. This density requires that the crystals at some stage of their existence were compressed by about 4%.

A combination of weak point-defect scattering, lack of resonant effects due to a broad spectrum of point defects, and relatively bad thermal conductivity in the pure materials suggests that the fluorite structure requires some further study. At present it is rather different from alkali halides.

V. SUMMARY

(1) Thermal-conductivity measurements have been made on CaF_2, SrF_2, and BaF_2, both in the pure state and when doped with a wide variety of point defects.

(2) The conductivity of pure SrF_2 and BaF_2 was lower than might be expected, but is difficult to understand in terms of limitations due to background chemical impurities.

(3) Li^+ and Na^+ impurities in all three hosts were seen to have no influence on the thermal conductivity. This is probably due to the low concentration (10^{18} cm^{-3}) of impurity. Failure to observe any effect at this concentration suggests that point-defect scattering is weak in these host materials.

(4) H^-, Sm^{++}, and U^{3+} point defects in CaF_2 were seen to scatter phonons by mass-difference scattering alone. No phonon resonances were observed, even at concentrations exceeding 10^{20} cm^{-3}. The strength of the scattering confirms the conclusion in point (3) above.

(5) H^-, Sm^{++}, and U^{3+} point defects in CaF_2 were also seen to produce a low-temperature thermal conductivity varying as T^3. This effect is tentatively ascribed to scattering by precipitates. Scattering of phonons from magnetic states was ruled out.

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Lifetime Studies on the Relaxed Excited State of Color Centers*

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The improved precision and accuracy of lifetime measurements allowed by the technique of detecting the single-photon delay distribution has been utilized in lifetime studies on F, M, and R centers in alkali halides. $\tau_R(F)$, the F-center radiative lifetime, was measured in KCl at 80°K and at different F-center concentrations. Even though the luminescence quantum yield η_R varies with concentration, $\tau_R(F)$ is shown to remain constant. This fact has been explained in terms of a tunneling process among nonrandomly distributed F centers. The radiative lifetime of excited M centers has been measured at 80°K in different alkali halides (in nsec): $\tau_R(M)=28\pm1$ in KCl; 26.2 ± 1 in NaCl; 17.2 ± 1 in LiF; 12.3 ± 1 in NaF. From the temperature behavior of $\tau(M)$ in KCl, the relaxed excited-state deexcitation energy ΔE_d has been evaluated: $\Delta E_d=0.21\pm0.01$ eV. The observed values of $\tau_R(M)$ and ΔE_d are discussed.

1. INTRODUCTION

Since Swank and Brown's early work[1] on the relaxed excited-state radiative lifetime $\tau_R(F)$, of F centers, considerable attention—both theoretical and experimental—has been devoted to certain problems common to F centers and to their aggregates M and R centers. These problems, which also constitute the general subject of the present paper, include (i) the exact energy-level scheme in the relaxed situation; (ii) the symmetry of the levels among which the emission transitions take place; (iii) the magnitude of τ_R and the influence on it of the host matrix and local relaxation; (iv) the possible influence of perturbations, such as foreign ions, concentration, and external fields. Our knowledge of the relaxed excited states of the F center and its aggregates is still unsatisfactory and not yet substantiated by conclusive statements. For instance, the proposals that have been made to explain the

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* A preliminary report on this work has been given at the 1968 International Symposium on Color Centers in Alkali Halides, Rome (unpublished).

[1] R. K. Swank and F. C. Brown, Phys. Rev. 130, 34 (1963).

magnitude of $\tau_R(F)$ range among "the large-orbit theory"[2] which gives maximum importance to the influence of relaxation and size of the orbit on the emission transition matrix elements; and the "forbidden transition theory"[3] which focuses the role of the $2s$ states in the emission process. Therefore, we thought it useful to obtain new and possibly more significant data on time-decay spectra of excited F, M, and R centers. Our interest was primarily concentrated in the following:

(i) on the time-decay spectra of excited F centers at different concentrations to detect possible effects due to nearby F centers. This could give some information about the extension of excited-state wave functions;

(ii) on the time-decay spectra of M centers in different alkali halides so as to observe the effect of the host matrix on $\tau_R(M)$.

As a matter of fact, measurements on the dependence of $\tau_R(F)$ from concentration have already been attempted,[4] and data on the radiative lifetime of both M and R centers in different alkali halides have been reported.[1,5–8] However, as it appears from Sec. 2, our lifetime measuring apparatus allows higher precision and reliability than previously used systems and therefore, a deeper understanding on the problems in which we are interested can be gained. Section 3 is devoted to reporting and briefly commenting upon the experimental data; in Sec. 4 a discussion of the tunneling mechanism for the F-center luminescence quenching is given, and the implications of the $\tau_R(M)$ and $\Delta E_d(M)$ data are commented upon.

2. EXPERIMENTAL PROCEDURES

The lifetime measuring apparatus is based on a method originating from the field of nuclear electronics: the basic idea is to measure the decay probability density as a function of time after excitation. This is done by exciting the sample with a pulsed light, detecting a single photon randomly selected between those emitted by the excited centers, and then measuring the time elapsed from excitation to detection. Repeating this procedure many times allows determination of the time-probability distribution with a precision increasing with the number of measurements.

Random selection of the emitted photons is achieved by lowering the excitation intensity until the probability of detecting a photon following excitation is quite low.

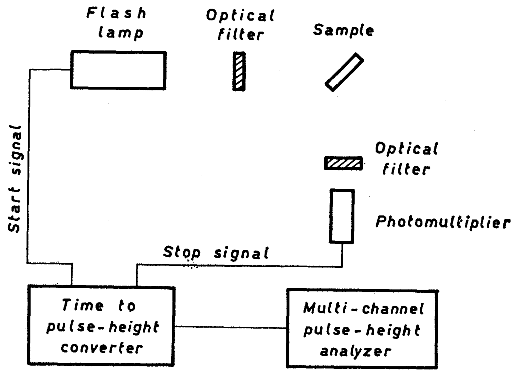

FIG. 1. Block diagram of apparatus.

In Fig. 1 a block scheme of the measuring apparatus is shown. The time elapsed between excitation and detection of a single photon emitted by the crystal is measured by using a time-to-amplitude converter and a multichannel pulse-height analyzer (LABEN Model No. 400). The start signal for the time-to-amplitude converter (TAC) is generated in correspondence to each light-exciting pulse; the stop signal is obtained, through suitable electronic circuits, from a 150 CVP Philips photomultiplier. This technique allows one to follow the exponential decay through many decades (3–4 or more) with a precision that, depending on the number of background pulses due to noise, is essentially limited by the duration of the measurements. The resolving power of the apparatus is limited by the exciting light source, consisting of a hydrogen spark lamp, which has a width of ~6 nsec at half-maximum and ~16 nsec at 10% of the maximum. In our present setup, therefore, lifetimes up to the order of 10^{-8} sec can be measured without unfolding of the noninstantaneous light source. Further details on the apparatus, which includes background subtraction facilities, will be given in a forthcoming paper by Bertolaccini *et al.*[9]

During our relatively long lifetime observations (lasting from 1–5 h) the temperature was stabilized, when needed, through an automatic system consisting of a thermocouple sensing element, an HP 741B differential voltmeter, and a simple electronic circuit controlling a heating element attached to the crystal holder. Temperature was stabilized within 1°K.

The alkali halide crystals, cleaved in thin slabs ($10\times10\times1$ mm), were mounted in our liquid-nitrogen stainless-steel cryostat. Before and after each lifetime measurement, absorption spectra were taken in a Cary-14 recording spectrophotometer in order to make sure that during the experiments no change had occurred in the system. Both additively colored and x-ray colored (at room temperature) KCl and NaCl crystals were used, while NaF and LiF were colored with x-ray irradiation (at room temperature). KCl crystals used for concentration-effect measurements

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

[4] H. V. Watts and G. A. Noble, J. Chem. Phys. **40**, 2051 (1964).

[5] A. M. Bonch Bruevich, G. A. Tischenko, and P. P. Feofilov, Opt. i Spektroskopiya **2**, 136 (1957).

[6] M. Nobile, Tesi di Laurea, Università di Milano (unpublished).

[7] F. Borms and G. Jacobs, Phys. Letters **27A**, 153 (1968).

[8] H. Mahr, in *Physics of Color Centers*, edited by W. Beall Fowler (Academic Press Inc., New York, 1968).

[9] M. Bertolaccini, C. Bussolati, and S. Cova (unpublished).

were carefully quenched (from 600°C) and mounted in the cryostat under a weak red safety light.

3. EXPERIMENTAL RESULTS

A. Radiative Lifetime of M and R Centers, $\tau_R(M)$ and $\tau_R(R)$, in KCl

In order to understand clearly the complex luminescence time-decay spectra observed (Figs. 4 and 8, curve *c*) in crystals in which F, M, and R absorption bands are present, it is necessary to identify the time-decay spectra of the excited state of F, M, and R centers. For this purpose, we optically converted F into M and R centers, at room temperature in a crystal in which the F-center concentration was 8×10^{16} F/cm^3 before conversion. Figure 2 shows the time-decay spectrum of luminescence in such a crystal after excitation in the M_1 band at 80 °K: $\tau_R(M)=28\pm1$ nsec. When the same crystal is excited either in R_1 or R_2 bands, time-decay spectra of the type shown in Fig. 3 are observed. Such spectra can be resolved into two simple exponential decays: the shorter one $[\tau_R(M)\approx30$ nsec$]$ is attributed to M centers, while the longer one $[\tau_R(R)=124\pm5$ nsec$]$ is due to R centers. It must be noted that, exciting both in R_1 and R_2 bands, the same excited R-center lifetime is observed. If we increase the temperature, the R-center luminescence yield decreases and reaches zero at about room temperature. At the highest temperature (252°K) at which $\tau(R)$ could be measured, it was ~10% shorter than at 80°K.

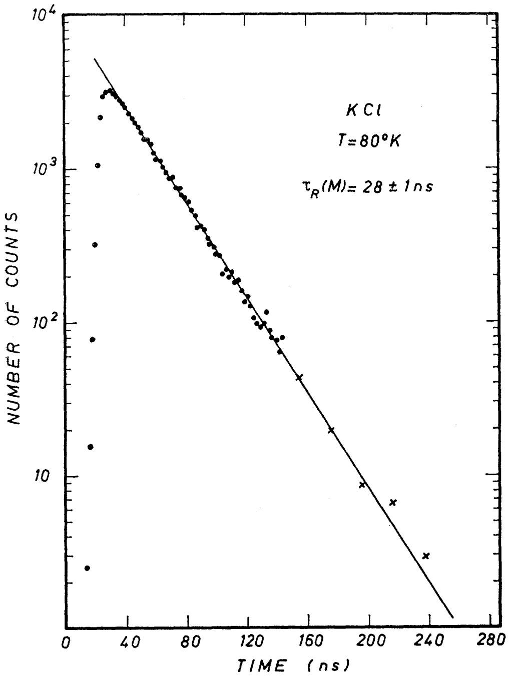

FIG. 2. Time decay of the luminescence excited at 80 °K in the M_1-band region of KCl; (little crosses represent averages over 10 channels). Optical filter in excitation: 800 mμ interference, Zeiss; in detection 87 A, Wratten Kodak.

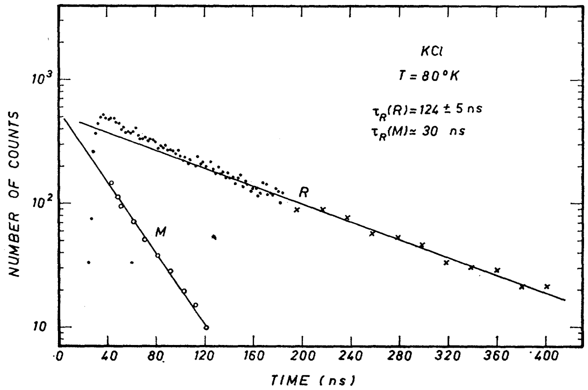

FIG. 3. Time decay of the luminescence excited at 80 °K in the R_2-band region of KCl; (little crosses as in Fig. 2). Optical filter in excitation: 725 mμ interference, Zeiss; in detection: 87 A, Wratten Kodak.

In Fig. 4 the time-decay spectrum for F-band excitation is shown. With the aid of spectra for this same experimental situation, but taken with a more expanded time scale, this spectrum can be resolved into three simple exponential decays. The shorter one shows the same lifetime $[\tau_R(M)\approx29$ nsec$]$ that is observed under M_1 absorption-band excitation, and therefore it can be attributed to M-center decay. The intermediate lifetime decay shows a lifetime $[\tau_R(R)\approx130$ nsec$]$ which is equal, within experimental errors, to that of the R center, and therefore, it can be attributed to R-center decay. As a matter of fact, it is well known that M- and R-center luminescence can also be excited in KCl when illuminated in the F absorption-band region. The slow decay, which has a lifetime equal to the one observed in crystals in which only the F absorption band is present (Fig. 8, curve *a*), is clearly due to F center's decay.

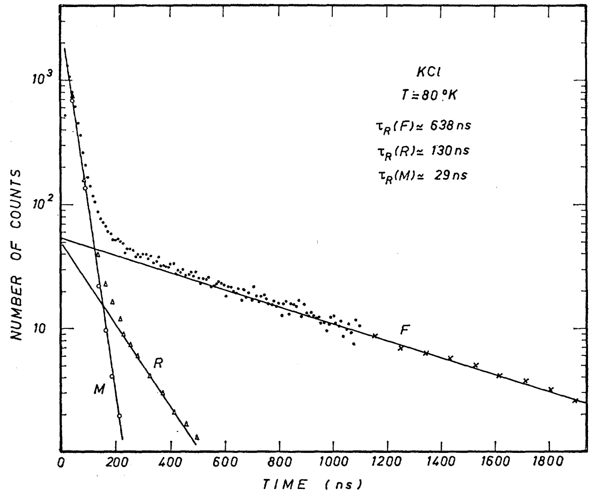

FIG. 4. Time decay of the luminescence excited at 80 °K in the F-band region of KCl; (little crosses as in Fig. 2). Optical filter in excitation: BG 18, Jenaer Glas Werke; in detection: 87 A, Wratten Kodak.

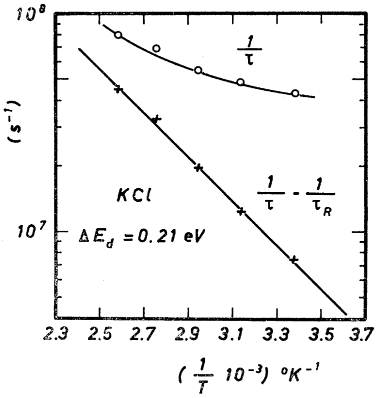

FIG. 5. Inverse lifetime versus inverse temperature for the M-centers luminescence in KCl. Luminescence deexcitation energy, $\Delta E_d = 0.21 \pm 0.01$ eV.

If we excite in the F band at room temperature, only the fast M-center's decay is present.

It can be observed that the M luminescence has the same lifetime, independent of the spectral region in which it is excited (that is in the F-, R-, or M_1-band region); this is consistent with the fact that only one emission band is observed. Upon increase of the temperature the excited M-center lifetime remains constant up to 200 °K. In Fig. 5 the variation of $1/\tau(M)$ versus $1/T$ is shown. If we suppose, as currently done for F centers, that $1/\tau(M) = 1/\tau_R(M) + (1/\tau_0) \exp(-\Delta E_d/KT)$, from the slope of $1/\tau(M) - 1/\tau_R(M)$, in which $\tau_R(M)$ is the low-temperature value of $\tau(M)$, we can calculate $\Delta E_d = 0.21 \pm 0.01$ eV.

B. Radiative Lifetime of M Center in NaCl, NaF, and LiF

Upon excitation of the M-center luminescence in the M_1 absorption band at 80 °K, as shown in Fig. 6, single exponential decays with $\tau_R(M) = 26.2 \pm 1$ nsec in NaCl, $\tau_R(M) = 17.2 \pm 1$ nsec in LiF, and $\tau_R(M) = 12.3 \pm 1$ nsec in NaF are observed. These values result from measurements performed on x-ray colored crystals, but the same value of $\tau_R(M)$ was obtained for NaCl with an additively colored crystal. At room temperature (300 °K) $\tau(M)$ in NaCl was nearly 1 nsec shorter than at 80 °K, in NaF 0.7 nsec shorter, and in LiF practically the same.

The time-decay spectrum of luminescence excited in the F absorption band of an x-ray-colored NaF crystal at 80 °K is shown in Fig. 7. This spectrum can be resolved into three simple exponential decays. The decay with longer lifetime, $\tau(F) \approx 53$ nsec, can be attributed to F centers[10]: The decay with intermediate lifetime, $\tau \approx 34$ nsec, is possibly due to R centers; the shorter decay, $\tau_R(M) \approx 12$ nsec, is due to M centers.

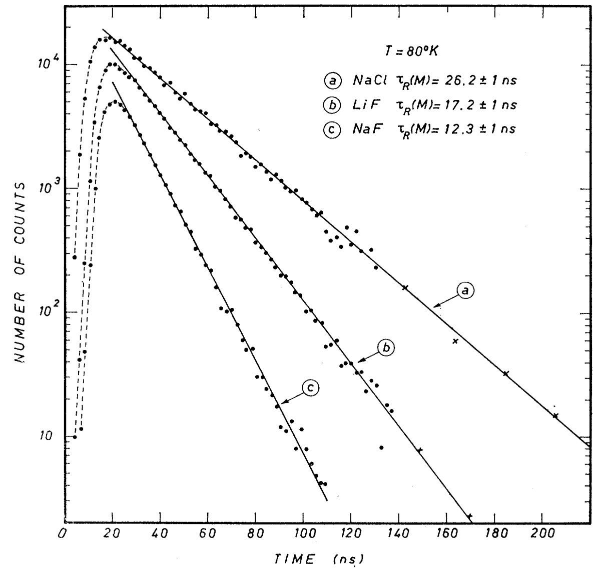

FIG. 6. Time decay of the M-center luminescence at 80 °K in NaCl (excitation filter: 725 $m\mu$ interference, Zeiss; detection: 87 A, Wratten Kodak), NaF (excitation: 500 $m\mu$ interference, Zeiss; detection: 650 $m\mu$ interference, Zeiss) and LiF (excitation: 450 $m\mu$ interference, Zeiss; detection: 675 $m\mu$ interference, Zeiss).

An entirely analogous situation was found upon excitation in the F band in NaCl at 80 °K. In this case the values obtained were: $\tau(F) \approx 266$ nsec,[1] and $\tau_R(M) \approx 24$ nsec, while the intermediate lifetime, which is possibly due to R centers, shows a lifetime $\tau \approx 56$ nsec.

C. Effect of F-Center Concentration of $\tau_R(F)$ in KCl

In Fig. 8 time-decay spectra of relaxed excited F centers for different F-center concentrations are shown. Such spectra were obtained by exciting freshly quenched additively colored crystals in the F absorption band; in the absorption spectrum of a and b specimens no

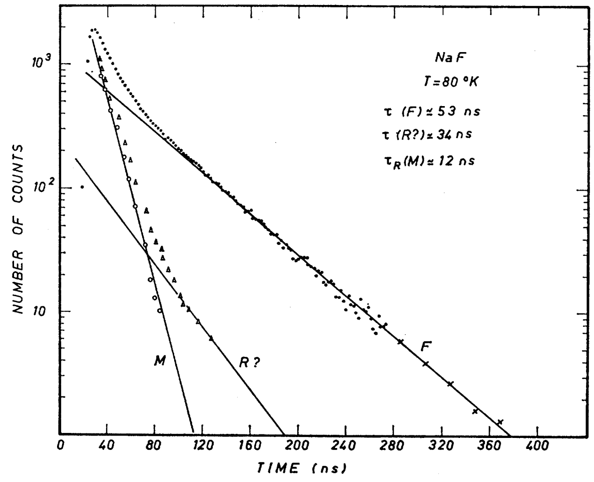

FIG. 7. Time decay of the luminescence excited at 80 °K in the F-band region of NaF. Optical filters in excitation: 331 $m\mu$ interference, Zeiss; in detection: RG 10 Jenaer Glas Werke.

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[10] L. Bosi, P. Podini, and G. Spinolo, Phys. Rev. **175**, 1133 (1968).

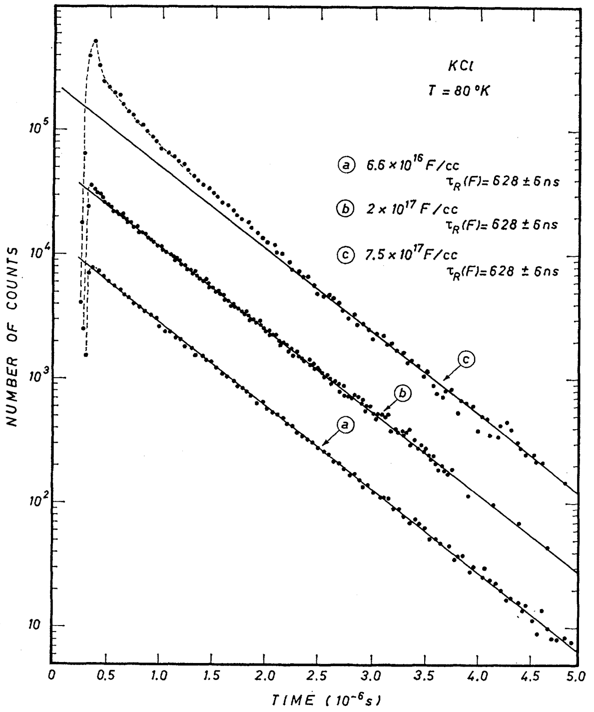

FIG. 8. Time decay of the luminescence excited at 80 °K in the F-band region for crystals with different F-center concentration.

absorption band other than the F one was noted, but in specimen c a small M_1 band was present.

A slow exponential decay which, without doubt, can be attributed to F-center emission, can be observed in all these time-decay spectra: its lifetime remains constant, within experimental errors, for the different F-center concentrations. The fast decaying components which become evident in the first part of time spectra at higher concentration, appear to be due, on the basis of the data shown in Sec. 3 A, to M and R centers. The excited F-center lifetime is therefore unaffected by F-center concentration. It is well known,[11] though, that concentration has a relevant effect on luminescence yield; at F-center densities similar to the one relative to curve c of Fig. 2, the yield is reduced down to $\sim 20\%$ with respect to the most diluted systems. These results are jointly discussed in Sec. 4 of the present paper.

Our measurements have also been performed on x-ray colored crystals and again $\tau_R(F)$ had, within experimental errors, the same value. It is, therefore, legitimate to compare $\tau_R(F)$ for various alkali halides, independent of the means used to introduce F centers into the specimen.[10]

4. DISCUSSION

A. Concentration Effect on $\tau_R(F)$

On the basis of the experimental results shown in Sec. 3 two main features of the decay of relaxed excited F centers appear evident. First, we note that the F-center decay is a single exponential over four decades in intensity, and so we feel more confident in describing the luminescent decay with the simple model employed up to now[1] and in excluding electron retrapping: such a process would, in fact, yield a complex time-decay spectrum.

Second, the lifetime of relaxed excited F centers appears to be independent of F-center concentration. This result, which is partly contradicting previous less accurate measurements,[1,12] looks rather puzzling when confronted with quantum-yield results[11] showing that η_R is considerably reduced at high F-center concentrations. Both results, however, can be explained on the basis of one of these two hypothesis: (i) a nonradiative deexcitation process due to the phonon emission, occurring during relaxation, takes place. Such a process can reduce the luminescence quantum yield, but it would not modify τ_R which depends on the temporal spectrum of the quanta coming from the relaxed excited-state radiative deexcitation. It seems difficult, however, to imagine how any feature of the relaxation around a center could depend on the F-center concentration. (ii) a nonradiative tunneling process from the relaxed excited state of an F center to a nearby one, occurs in a nonuniform distribution of centers.

Up to now, under the hypothesis of a uniform statistical distribution of centers, some authors[11,13] have done experiments to obtain the average distance necessary to have electron tunneling among F centers, the values obtained ranging between 35 Å and 80 Å.

We think, on the contrary, that, since there is no concentration effect on $\tau_R(F)$, the tunneling process is not a decay channel which belongs to each relaxed excited F center. We suggest that, at high F-center concentrations, for some centers tunneling has probability 1 to occur, while for other centers far apart from each other, this probability is practically zero. Since the centers we are studying are those which emit, their tunneling probability is zero, and for them no concentration effect on $\tau_R(F)$ is found. A concentration effect is observed on η_R since some of the F centers which have been excited do not emit, but are deexcited through a two-step nonradiative process in which tunneling has the role described by Chiarotti and Grassano.[13] We have no way to analyze quantitatively our data and obtain a value of the distance between two F centers required to give tunneling of the excited electron with subsequent luminescence quenching. We may, however, think that the distance for tunneling should not exceed

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[11] A. Miehlich, Z. Physik **176**, 168 (1963).

[12] If we note that we have made the lifetime measurements with an oscilloscope (thereby examining reliably a maximum of 2 decades), and inspect Fig. 8, we immediately realize that at high concentrations the fast components $M+R$ are the main contributions to the time-decay spectrum.

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

1 or 2 lattice constants; otherwise, the sharp discontinuity in tunneling probability could not be understood. Tunneling, in fact, depends essentially on the thickness of the barrier (of the distance among the centers interested in the tunneling). A smooth distribution of distances among nearby centers (such as would occur if the center distribution is uniform and the average distance between centers is of the order of many lattice parameters) would not explain the strong change in tunneling probability which has been assumed in order to explain our experimental results.

B. Lifetime of the Relaxed Excited *M* Centers

The decay of relaxed excited *M* centers, according to our experimental results, is characterized by a single exponential. $\tau_R(M)$ is independent of the particular absorption band (M_1, M_2, M_3, or M_4) in which luminescence has been excited. This fact is in accordance with already known measurements of the emission spectrum[14] which shows only one emission band. This behavior, which is also shown by *F* centers (for which there is only one emission band common to *F*- and *K*-band excitation), by *R* centers, as previously observed, and by F_A centers (apart from doubts recently cast by some authors[15]), confirms the simple model of only one relaxed excited energy level involved in the emission process.

In the notation of molecular spectroscopy, emission is due to a $^1\Sigma_u \rightarrow {}^1\Sigma_g$ transition. As far as the measured lifetimes are concerned, our values relative to NaCl and KCl, are considerably shorter than previously measured ones[1,6,7]; excellent agreement exists with data on LiF and NaF obtained with the phase-shift technique.[5] The short value of observed lifetimes and the smaller values of the Stokes shift, when compared with the ones relative to *F* centers, suggest a rather compact relaxed excited *M*-center model.

A theoretical estimate of $\tau_R(M)$ for KCl[16] based on the Einstein coefficients approach was made, and one can observe that, to the contrary of the *F* center's estimate, here the theoretical estimate of the lifetime is longer than the experimental value (by a factor of 2). This discrepancy is probably due to the lattice relaxation, which causes considerable changes in the wave functions involved in the emission and absorption processes.

To understand the influence of the host crystal on $\tau_R(M)$, we may search for an intrinsic parameter of the matrix to plot $\tau_R(M)$. It would be interesting to see how the ratio of absorption to emission matrix elements in the Einstein-coefficients formula[16] changes as a function of the various host crystals, and evaluate the effect of the different relaxations on τ_R; but, unfortunately, the oscillator strength of the M_1 band is known only for KCl. A straight-forward relation with the lattice parameter *d* does not help either, since in the *d*-values sequence NaF is not an extremum, but, for the *M* centers, as well as for the *F* centers, NaF has the shortest lifetime.

In the present work we have also measured the ΔE_d for the relaxed excited state of the *M* center in KCl; it turned out to be ≈ 0.21 eV. Since, in the other alkali halides we studied, $\tau_R(M)$ was practically constant up to 300 °K, we suppose that in NaCl, NaF, and LiF, ΔE_d is of the same magnitude or greater. The value of ΔE_d we report is quite smaller than that of ΔE_d and ΔE_i obtained by other authors through quantum yield[17] and photoconductivity[17,18] measurements, respectively; for them $0.30 < \Delta E_i < 0.40$ eV and $\Delta E_d = 0.38$ eV. The quantum-yield data are perturbed by the disappearance of centers during the measurement and, therefore, the ΔE_d value obtained in such a way cannot be entirely trusted.

If we do not have sound reasons to cast doubts on ΔE_i data, we are forced for the moment to suppose that there is at least another excited level between the conduction band and the relaxed excited level whose lifetime we have just measured. A similar proposal has already been made to explain certain peculiarities of the emission of alkali fluorides[10]; excited-state spectroscopy seems to be the best technique with which to tackle this problem.

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[14] Ch. J. Delbecq, Z. Physik **171**, 560 (1963).

[15] M. Tomura, T. Kitada, and S. Honda J. Phys. Soc. Japan **23**, 1179 (1967).

[16] W. B. Fowler and D. L. Dexter, J. Chem. Phys. **43**, 1768 (1965).

[17] M. Hirai and K. Hashizume, J. Phys. Soc. Japan **24**, 1059 (1968).

[18] N. Barth, Z. Physik **149**, 370 (1957); W. D. Compton and H. Rabin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, p. 205.