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Luminescence and lifetimes of *L* resonant states in alkali halides

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The time behavior of the fast luminescence produced by excitation in the *L* bands has been studied in KCl crystals, additively *F* colored. The results obtained show that the luminescence emitted in the temperature range 30–130 °K is characterized by the lifetime typical of the *F* excited relaxed state. A model has been proposed for the decay from the *L* states to the *F* excited relaxed state, from which the luminescence takes place. A second deexcitation process is the tunneling *L* state–conduction band. This model should be valid for all the alkali halides. From the quantum yields of the luminescence excited with *L* lights, the fraction of the electrons relaxing to *F* excited state and the fraction of the electrons freed in the conduction band have been determined. Finally, the order of magnitude of the resonant-state lifetime is determined.

I. INTRODUCTION

As is known, some absorption bands are associated with the *F* center[1] in the alkali halides: the *F*, the *K*, and, at higher energies, the *L* bands (L_1, L_2, and L_3, respectively).[2,3] These latter correspond to weakly allowed transitions, characterized by an oscillator strength[2] that in KCl ranges from 0.005 to 0.02, while to the *F* and *K* bands in KCl are associated oscillator strengths of 0.85 and 0.11, respectively. The *F* band is due to the transition from the ground state to the first excited state of the *F* center; the transitions to the higher excited states give rise to the *K* band. Some of these last levels are so near to the ionization bottom that at low temperature the electron is free in the conduction band.[4,5] Because the *L* states are at energies higher than the *K*, they should be located at energy values typical of the conduction band. Actually, *L* light can be used successfully for $F \rightarrow F'$ conversion at low temperature, where, using *F* light, such a conversion cannot be obtained.[6] The quantum yield of producing conduction electrons with *L* light has been investigated in two photoconductivity measurements[4,5] with different results. In the first work[4] the results show that most of the electrons are free in the conduction band (the quantum yield for the photoconductivity is close to unity), while in the second work[5] only a few electrons are free (the quantum yield is of the order of 0.04).

Optical measurements state that the same emission is obtained with *F*-light and *L*-light excitation. However, each quantitative conclusion is difficult because of the low intensity of the emission after *L* excitations. Lüty gives for the absolute quantum yield of this emission[2] a value of about 0.1.

From a theoretical point of view the properties of the shallow impurity states in semiconductor materials have been investigated with the "effective-mass approximation."[7] When deep levels are considered, a reformulation of the impurity problem is necessary to give more precise information. In this general formulation[8] extended also to insulating materials, bound states or resonant states above ionization in correspondence to critical points of the band structure can be found. These states (among which the *L* states can be included) are similar to the resonances of the scattering theory, but they arise from the band structure rather than from the nature of the potential. The lifetime of these states should be extremely short (of the order of 10^{-15} sec if determined with the scattering theory)[9] in comparison with the lifetimes associated with the usual radiative decay processes.

The purpose of this work is to complete the knowledge of the electronic processes that follow the absorption of L_1, L_2, and L_3 light. The time behavior of the luminescence signals has been studied in order to determine the lifetime of the state from which the luminescence takes place after excitation with *L* light, and in order to determine the time of filling up of this state. From the area of these signals with and without an $F \rightarrow F'$ conversion another interesting piece of information can be deduced as discussed below. Lifetime measurements with only L_1 light have been published in a previous paper.[10] In this work they are extended to include the case in which F' and α centers are present.

II. EXPERIMENT

Crystals of KCl were grown in our laboratory and additively colored. After mounting in the cryostat under red safety light, spectrophotometers Cary 14R and Cary 14 were used in order to determine both the *F*-center concentrations and

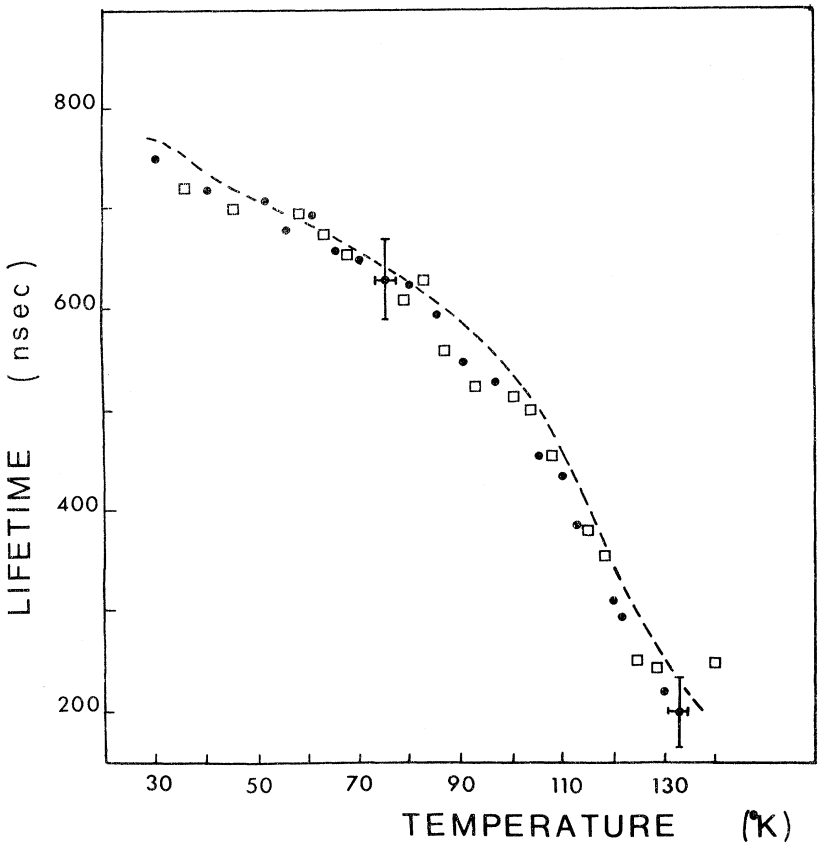

FIG. 1. Temperature dependence of the luminescence lifetime in KCl with *F* centers. □, the excitation with L_2 light; ● the excitation with L_3 light. Dashed line represents the lifetime excited with *F* light as deduced from Ref. 10. The *F*-center concentration ranged between 5×10^{16} and $5\times10^{17}/\mathrm{cm}^3$.

the presence of other kinds of color centers. The time behavior of the luminescence signals was studied by means of equipment previously described.[11] The spark lamp was filled with nitrogen or hydrogen gas. In order to select L_2 and L_3 lights, interference filters (Baird Atomic) starting from the spectral regions centered, respectively, at 2500 and 2850 Å were used. L_1 light was obtained using Jena-Schott interference filters with the maximum transmission at 3400 Å and nearby regions, combined with the broad-band glass filters BG-18 (Jena-Schott) in order to avoid higher harmonics. At the output of the system before the photomultiplier tube a cutoff filter (for example, 7-56 Corning) was used in order to avoid the transmission of the lamp light in the ultraviolet and visible region. Care was taken in order to use under these experimental conditions filters with a transmission ratio in the *L* and *F* regions, higher than 10^5, so a contribution of the *F* absorption band can be neglected. The measurements are hard because of the low intensity of the emitted light.

Moreover, the following test was performed. An *F* filter was added to each *L* filter. In this way the *F* light transmitted by the *L* filter passes practically unreduced in intensity, while the *L* component is reduced by some orders of magnitude. In these conditions we have no luminescence. A similar test was performed after the $F\rightarrow F'$ conversions to ensure that no detectable F' excitation took place in the region between 7000 and 13000 Å. For example, a RG-10 (Jena-Schott) glass filter added to the *L* filter allows the transmission between 7000 and 13000 Å of the same light that passes with the *L* filter, but reduces by some orders of magnitude the *L* light. No detectable contribution of excitation between 7000 and 13000 Å was found at any degree of $F\rightarrow F'$ conversion.

III. RESULTS

The experimental results are the following.

(a) As shown in Fig. 1, the behavior of the luminescence lifetime versus temperature is the same both with L_2 and L_3 excitation light and with *F* light, in the limit of the experimental errors that can be estimated as 6% at low temperature and 15% above 120 °K. The rise time of the luminescence signal is the same as that of the excitation source, i.e., the order of some nanoseconds.

(b) If in the crystal an $F\rightarrow F'$ conversion is made (by irradiation in the *F* band at a temperature of about 170 °K) two effects are observed. An increase of the luminescence lifetime excited by *L*

TABLE I. Relative quantum yield of the luminescence excited with L_1, L_2, and L_3 light (a.u.). The F-center initial concentration is $2.36\times10^{17}/\mathrm{cm}^3$, converted: $7.2\times10^{16}/\mathrm{cm}^3$ F centers.

with F' and α centers	without F' and α centers
$L_1 = 31$	$L_1 = 9$
$L_2 = 52$	$L_2 = 17$
$L_3 = 42$	$L_3 = 8$

light is observed for each given $F \rightarrow F'$ conversion. This lifetime is the same as that obtained with F-light excitation.[12] This result is further evidence that the emission excited with L light arises from the F excited relaxed state ($\tilde{F}^*$) and that the increased lifetime of the luminescence is that of $\tilde{F}^*$, in the presence of α (or F').

The relative quantum yield of the luminescence signal (excited with L light) increases in the presence of α and F' centers (see an example in Table I).

IV. DISCUSSION

The results sketched above suggest that the emission following the L-light excitation is the typical emission of the F excited relaxed state. It is possible on the basis of these new results and of the results previously reported[1–6,8,10] to support and extend the following picture of the electronic processes after excitation with L light. Figure 2 gives a qualitative representation of these processes in order to achieve a better understanding. The electron excited by L light reaches [(a) in Fig. 2] the L states that are in resonance with the conduction band and it is possible to exclude that all these electrons are freed in the conduction band. In fact, the F centers excited by the lamp during each of our sets of measurement are some orders of magnitude (about four or five) less than the F centers present. Therefore the α centers created by the excitation of the F centers are of the same order of magnitude, if we suppose that all the electrons are freed in the conduction band. Assuming a cross section for the α center about 20 times higher than the F-center cross section,[13] the probability that the free electron will be captured by an α center giving luminescence is about 500 times less than the probability that the electron will be captured by an F center. We have calculated that the luminescence signal obtained under this condition should be two orders of magnitude smaller than the luminescence signal really observed in our measurements.

Moreover, if the radiative decay should come exclusively from the capture of free electrons, one should have an emission intensity which depends on the light dose, starting from a very low value and increasing linearly at least in the first stage of irradiation.[10] The conclusion is that the luminescence observed is obtained when an electron excited by L light returns to the same center which undergoes the absorption of the quantum of light.

An electron in the L state should have two possible channels for the deexcitation process: a nonradiative tunneling to the conduction band [(b) in Fig. 2], as suggested by the photoconductivity measurements[4,5] and by the $F \rightarrow F'$ conversion[6]; and a nonradiative fast decay from the L state to the F excited state [(c) in Fig. 2].

In the first case the tunneling probability seems independent of the temperature[10] up to about 100 °K, and the electron freed in the conduction band is captured only by the F centers if the number of α centers is much smaller than the number of F, as in our experimental conditions.

In the second case most of the energy is lost in nonradiative processes and the electron reaches the F excited state along a configurational coordinate in a time less than 10^{-8} sec, as the rise time of the luminescence signal shows.

Two questions are now to be answered: (a) the quantum yield of the radiative emission, that is, the fraction of electrons coming back to the F ex-

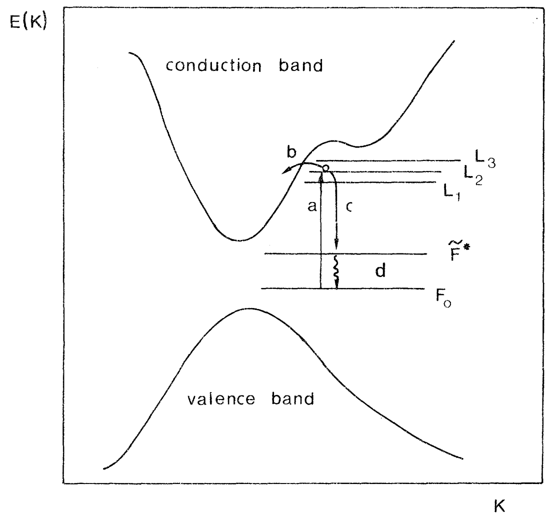

FIG. 2. Schematic representation of the electronic transitions after L-light excitation. (a), transition following L_2 light absorption from ground state to L_2 state; (b), tunneling to the conduction band; (c) nonradiative relaxation from L_2 state to the F excited state; (d), radiative transition from F excited relaxed state to the F ground state.

cited state; (b) the value of the lifetime of the L resonant state.

These points can be partially clarified with the analysis of the luminescence signals obtained in the presence of a high concentration of α centers. If a controlled $F \rightarrow F'$ conversion is made in the crystal the electrons freed in the conduction band "see" a number of α centers of the same order of magnitude of the number of F centers present. Under these conditions the electrons in the conduction band are no longer captured only by the F centers, but also by the α centers in a ratio depending on the relative concentrations of these centers and on their capture cross sections. These last, as is known, are a function of the temperature.[5,13,14]

Therefore, in the presence of α centers an increase of the luminescence quantum yield should be obtained. The luminescence signals are measured at liquid-nitrogen temperature (LNT) with L_1-, L_2-, and L_3-light excitation both when only F center are present and when F centers plus α centers are present in the crystal. The areas of the luminescence signals (that are proportional to the relative quantum yields) are reported in Table I for a case in which the initial F-center concentration is $2.36\times 10^{17}/\text{cm}^3$.

If we consider only F centers present in the crystal and neglect the α-center number created during the measurement with respect to the F-center number, it is possible to write

$$A = \mu(L) n x \;,$$

where A is the area of the luminescence signal (that is, proportional to the relative quantum yield of luminescence at LNT), $\mu(L)$ is the absorption coefficient for the L transitions, n is the number of the lamp photons in the L band, and x is the fraction of the electrons coming back to the F excited state (that is, the electrons that give luminescence at LNT).

If we consider F centers plus α and F' center, one has instead

$$A' = \mu'(L) n x + \mu'(L) n(1-x)\gamma + \mu(F') n\gamma \;,$$

where $\mu'(L)$ is the new absorption coefficient for the L transitions after the $F \rightarrow F'$ conversion, $\mu'(L)n(1-x)$ are the electrons that tunnel from the L states to the conduction band, and $\mu(F')$ is the F' absorption coefficient under the L bands. $\gamma = \sigma_\alpha N_\alpha / \sigma_\alpha N_\alpha + \sigma_F N_F$ is a coefficient that takes into account how many electrons freed in the conduction band are captured by α centers, σ_α and σ_F are the electron capture cross section for α and F centers, N_α and N_F are the concentration of α and F centers, respectively.

The ratio A'/A becomes

$$A'/A = \frac{\mu'(L) n x + \mu'(L) n(1-x)\gamma + \mu(F') n\gamma}{\mu(L) n x} \;. \qquad (1)$$

The data of Lüty[2] and Lynch and Robinson[15] have been used for the absorption coefficients of L bands and F' bands in the L region. Knowing the α- and F- center concentrations and σ_α and σ_F,[13] from the ratio of the quantum yields A and A' (if expressed in arbitrary units) it is possible to obtain the parameter x. The values found at LNT for L_1-, L_2-, and L_3-light excitations are, respectively,

$$x_1 = 38\%, \quad x_2 = 26\%, \quad x_3 = 12\% \;.$$

Taking in account the errors in the determination of the lifetime and of the number of α centers, the error in x can be estimated to be of the order of 15%.

The last comment we can make on the basis of the previous results concerns the lifetime of the L resonant states.[16] Because the electron in the L resonant state has two channels for the deexcitation process, the following expression should hold:

$$x\,\tau_{\text{rel}} = (1-x)\,\tau_{\text{tunn}} \;, \qquad (2)$$

where τ_{rel} is the time for the relaxation process from the resonant state to the F excited state and τ_{tunn} is the time for the tunneling process from the resonant state to the conduction band. If the electron excited to the L state comes back to the F excited state along a configurational coordinate, as in our hypothesis, the time for the relaxation process is usually assumed to be of the order of 10^{-12} sec. Therefore the τ_{tunn} can be calculated from formula (2). The following three values have been obtained:

$$\tau_{\text{tunn}}(L_1) \simeq 6\times 10^{-13} \text{ sec} \;,$$

$$\tau_{\text{tunn}}(L_2) \simeq 3\times 10^{-13} \text{ sec} \;,$$

$$\tau_{\text{tunn}}(L_3) \simeq 1\times 10^{-13} \text{ sec} \;,$$

where the L_1, L_2, and L_3 symbols in parentheses indicate the L light with which the electron has been excited to the resonant state. It is now possible to determine the order of magnitude of the lifetime $\tau(L)$ of the resonant state itself. In fact, we have

$$1/\tau = 1/\tau_{\text{rel}} + 1/\tau_{\text{tunn}} \;,$$

and inserting the values previously obtained $\tau(L)$ results in

$$\tau(L_1) \simeq 4\times 10^{-13} \text{ sec} \;,$$

$$\tau(L_2) \simeq 2\times 10^{-13} \text{ sec} \;,$$

$$\tau(L_3) \simeq 9\times 10^{-14} \text{ sec} \;.$$

In conclusion, from the experimental data of fast luminescence excited by L light a model has been developed for the electronic transitions following the absorption of L light. A fraction of the electrons raised to the L state comes back to the F excited state, giving luminescence. This fraction ranges between 10 and 40%, according to the L state we consider. It is worthwhile to stress that these values are considerably higher than is usually assumed in the current literature.

From these data the order of magnitude of the lifetime of the L state can be determined as 10^{-13} sec. This result seems to agree with the conclusion of Ref. 8, which states that the lifetime of the resonant states produced by the structure of the conduction band should be longer than the lifetime of resonant states considered in scattering theory, which is of the order of 10^{-15} sec.[9]

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[1] G. Chiarotti and U. M. Grassano, Nuovo Cimento B 46, 78 (1966).

[2] F. Lüty, in *Halbleiterprobleme*, edited by W. Schottky (Vieweg, Braunschweig, West Germany, 1961), Vol. 6.

[3] M. Hirai and M. Ikezawa, J. Phys. Soc. Jpn. 22, 810 (1967).

[4] F. Nakazawa and H. Kanzaki, J. Phys. Soc. Jpn. 22, 844 (1967).

[5] R. L. Wild and F. C. Brown, Phys. Rev. 121, 1296 (1961).

[6] M. Hunger and F. Lüty, Phys. Lett. 15, 114 (1965).

[7] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 257.

[8] F. Bassani, G. Iadonisi, and B. Preziosi, Phys. Rev. 186, 735 (1969). G. Iadonisi and B. Preziosi, Nuovo Cimento B 15, 45 (1973).

[9] F. Bassani (unpublished).

[10] S. Benci and M. Manfredi, Solid State Commun. 9, 1255 (1971).

[11] S. Benci, P. A. Benedetti, and M. Manfredi, Rev. Sci. Instrum. 41, 1336 (1970); 45, 438 (1974).

[12] S. Benci and M. Manfredi, Phys. Rev. B 7, 1549 (1973).

[13] J. J. Markham, in *Solid State Physics*, Suppl. 8, edited by F. Seitz and D. Turnbull (Academic, New York, 1966), p. 132.

[14] An interesting work on capture cross section, if the material studied is KBr instead of KCl, is R. S. Crandall, Phys. Rev. 138, A1242 (1965).

[15] D. W. Lynch and D. A. Robinson, Phys. Rev. 174, 1050 (1968).

[16] M. Fontana (private communication). Y. Farge and M. Fontana, *Perturbations êlectroniques et vibrationelles localisêe dans les solides ioniques. Collection de monographies de physique* (Masson et Cie., Paris, 1974).