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Some effects of perturbation on F-centre lifetime

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Résumé. — Des mesures de luminescence indiquent un remarquable accroissement du temps de vie moyenne des centres F dans KBr en fonction de la température, en correspondance de valeurs critiques de la concentration de centres α, après conversion F → F' + α.

L'analyse de ces données est effectuée en tenant compte aussi des expériences de photoconductivité par Crandall. On interprète les résultats expérimentaux dans le cadre d'un mécanisme d'interaction qui entraîne la section de capture des électrons par le centre α et la distance moyenne entre les centres F.

En particulier, la montée de la valeur du temps de vie moyenne, qu'on remarque à peu près à 65 K, est en relation avec des concentrations de centres α assez faibles et dans quelques cas à peine détectables. De plus, en examinant les expériences décrites dans la littérature scientifique, on remarque que dans le cristal employé on a toujours une quantité de centres α pas tout à fait négligeable.

Tous ces faits nous entraînent à formuler une hypothèse nouvelle, qui pourrait résoudre la longue querelle sur la nature de l'état excité relâché : les valeurs du temps de vie moyenne des centres F mesurés à températures suffisamment basses pourraient être fausses, à cause de la perturbation apportée par l'interaction entre les centres F et α.

Abstract (*). — Luminescence measurements show a temperature-dependent increase in F-center lifetime in KBr, corresponding to critical α-center concentrations, after F → F' + α conversion.

Data analysis has been made in connection with the Crandall photoconductivity experiments and the results are explained on the basis of an interaction mechanism that involves the electron-capture cross-section by the α-centers and the mean distances between the F-centers. In particular, the increase in the lifetime, at near 65 K, is related to low and, in some cases, scarcely detectable α-center concentrations. Furthermore, analysis of experiments known in literature reveals that a far from negligible quantity of α-centers is always present in real crystals.

These effects lead us to a new stimulating hypothesis which can resolve the up-to-now intriguing discussion on the nature of the relaxed excited-state : the observed lifetime values at a sufficient low temperature might be incorrect because of the perturbation due to the interaction between F- and α-centers.

1. Introduction. — The lifetime \( \tau_R \) of the relaxed excited state (RES) of the F center in alkali halides has been accurately studied and its values are well-known in the literature [1]; furthermore, as for the F-emission energies [2], some general correlations with optical parameters have been found by us [1]. Experiments involving perturbations have been carried out in order to obtain information on the RES : the small decrease in \( \tau_R \), due to the presence of a substitutional neighbouring alkali ion (F\(_A\)-center), evidences a spread wave-function [3]; stress measurements [4] do not reveal an appreciable effect on \( \tau_R \)-values; ESR experiments [5, 6] are once more in agreement with the hypothesis of a diffuse RES. Nevertheless, the effects of applied electric fields have been interpreted by Bogan et al. [7] in terms of nearly degenerate s- and p-like states; this model seems to explain the increase in \( \tau_R \) (whereas the relative quantum yield, \( \eta_R \), is constant) in the low-temperature range (roughly, below LNT).

Ham et al. tried to explain all the above experiments on the basis of a vibronic model [8, 9]; on the contrary, in a very recent theoretical work, Markham et al. [10] criticize Ham's model and the Bogan's explanation of his results on the electric field effect.

As regards the problem of the luminescence occurrence from F-centers in alkali halides, Bosi et al. [11] have discussed the validity of the models based on the traditional Franck-Condon scheme, and have shown [12] that \( \tau_R \) values are independent of F-center concentration, although Miehlich [13] has observed a decrease in the absolute quantum yield.

The aim of this paper is to present the results of our recent works [14, 15] on the α-centers interaction together with a discussion of several experiments on color center physics, pointing out that a far from negligible quantity of α-centers is always contained in real crystals. We will propose a new explanation of the \( \tau_R \)-change in the low temperature-range on the basis of an interaction mechanism between F- and α-centers.

(*) Footnote : Abstract and text contain data and conclusions over and beyond those included in the conference booklet : indeed, several results had not been achieved at the time of the call by the Conference Secretary.
2. Experimental results and discussion. — Lifetime data have been obtained by means of our traditional SPDD technique [1, 12, 14, 15].

Details of the experiments in KBr samples, containing F- centers, have been given in the previous papers [14, 15] to which interested readers are referred. In particular, we started by considering the Crandall’s photoconductivity experiments [16] when the reciprocal of the product of the conduction band lifetime, mobility and \( n \)-concentration is plotted versus \( N_F/N_a \), for low \( F \)-density samples (i.e., at near 81 K, in a sample containing practically the a-critical distance to be lower than the a-critical distance). For these reasons, we may assume that \( N_F/N_a \) is independent of the \( F \rightarrow F' \) conversion for \( N_F/N_a > 8 \), and is the same as in unbleached samples.

A sudden increase in \( \tau_R \) (see Fig. 1 of ref. [14]) is observed for \( N_F/N_a < 8 \), whereas Crandall photoconductivity becomes non-linear when \( N_F/N_a > 14 \). For example, \( \tau_R \) changes from 1230 up to 1750 ns at \( N_F/N_a \approx 3 \) (i.e., a practically undetectable concentration). Initially, we performed [14] lifetime measurements, at near 81 K, in a sample containing practically the same concentration used by Crandall. The most important features are the following:

i) \( \tau_R \) does not appreciably change when \( N_F/N_a > 8 \), whereas a sudden increase is observed when \( N_F/N_a < 8 \) (for example, \( \approx 51 \% \) at \( N_F/N_a \approx 2.6 \)).

To explain our results, it may be remembered that the \( \alpha-F \) interaction is of monopole-dipole type [17, 14]. For these reasons, we can expect the interaction critical-distance to be lower than the \( \alpha \)-critical distance in the Crandall experiment (where interaction between a positive charge and a free electron is studied). As a consequence, these data strongly support the hypothesis of a sudden interaction effect for which \( \sigma_\alpha \)-overlap must occur and the relative distances between the centers reach a very critical value. In our opinion the observed increase in \( \tau_R \) can be explained on the basis of the following factors: a decrease in the emission dipole matrix element \( \langle \pi \rangle \) due to RES wavefunction spread and a decrease in the effective electric field [18, 14] (from the Lorentz to the average one). The effect in \( \eta_R \) can be explained by assuming an inhibition of the luminescence quenching at high F-densities, in agreement with Miehlich’s results [13] in KCl: when \( \sigma_\alpha \)-overlap has reached a critical value, tunnelling between F-..-centers does not take place. However, we must remember that \( \tau_R \) values are \( F \)-density independent in unbleached samples. As discussed in a previous paper [14], spurious effect due to F- and F'-band overlap, or to F'-bound states can be disregarded.

More recent measurements [15], performed at near 65 K, show the following features:

a) An increase in \( \tau_R \) values is observed in high \( F \)-density samples for every optically detectable \( \alpha \)-concentration (see Table I of ref. [15]). An increase in \( \eta_R \) has also been unambiguously found.

b) An increase in \( \tau_R \) is observed in low \( F \)-density samples, only at high \( F \rightarrow F' + \alpha \) conversion.

These results are in agreement with the above discussion: indeed, because of the strong temperature dependence of \( \sigma_\alpha \), changes in \( \tau_R \) can be observed at low conversions. As regards point b), high conversions are indispensable to have a sufficient \( N_a \) and \( \alpha \)-centers to be considered. Let us discuss, now, the possibility that \( \tau_R \) values, at low \( T \), may not be intrinsic.

Changes in \( \tau_R \) have been also observed in KCl [19, 20], in the presence of \( \alpha \)-centers. Hoffmann [21] et al. revealed an appreciable \( \alpha \)-quantity frozen-in in KBr samples. Data on the electron Hall mobility can be explained only if the scatterer is a charged center [22, 23]. Hall mobility dependence on magnetic fields applied [23] cannot be explained by the presence of \( F \)-centers, which are neutral. Furthermore, the mobility is reduced, at 7.7 K, after \( F \rightarrow F' + \alpha \) conversion [23]: a close agreement with the Conwell-Weisskopf formula [24] for the scattering of charged impurities has been found [23]. For example, mobility in KBr samples containing \( 2 \times 10^{16} \) F/cm\(^3\) could be explained by the presence of about \( 6.5 \times 10^{13} \) a/cm\(^3\) (i.e., a scarcely detectable concentration).

Low-T photoconductivity data [25, 20] can hardly be explained by the usual two-level model for the F-decay.

In conclusion, \( \alpha \)-densities seem to be far from negligible in every experiment on color center physics: moreover, at low-\( T \), \( \sigma_\alpha \)-overlap fills in the whole sample. As a consequence, we may assume that \( \tau_R \) values could be not intrinsic.

The above discussions on the \( \alpha-F \) interaction have been implicitly carried out on the basis of the large orbit theory [27] for the RES.

We want to emphasize that a Rydberg law was found by us [2] for the emission energies of F-centers:

\[
(E_{2p} - E_{1s}) = -\frac{e^4 m^*}{2 \hbar^2 e_m^2} \left( \frac{1}{2^2} - \frac{1}{1^2} \right) = \frac{10.15}{e_m^2} m^*. 
\]

We notice that not only the functional dependence but also the value of the constant appears to be verified. Moreover, by inserting it in the traditional Fowler-
Dexter formula [27] for the lifetime, we found [1]:

$$\tau_R = A e^{5.5} \left| \langle r \rangle \right|^2_{\text{lem}}$$

whereas experimental data are fairly well interpolated [1] by the function $$\tau_R = K e^{5.5}$$.

In this way, $$\left| \langle r \rangle \right|^2_{\text{lem}}$$ seems to be the same for every alkali halide investigated.

Our results are in close agreement with recent ESR measurements [6]: the RES wavefunction in various crystals is very diffuse and approximately the same when scaled with the lattice constant; the wavefunction parameter is very similar to that used by Fowler [27].

In conclusion the increase in $$\tau_R$$ in the low temperature range, might not be an intrinsic effect; indeed, even a very small change in the wavefunction parameters (due to the interaction with the a-centers frozen-in in the sample) strongly [1] affects $$\tau_R$$.

As a consequence RES models based on 2s-2p mixing should be revised.

References