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Evidence for the interaction between the free exciton and the F^- centres in KI

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Résumé. — Le signal de luminescence résonnante observé à 2 125 Å dans KI irradié aux électrons à très basse température augmente lorsque le cristal est éclairé par de la lumière infrarouge. Ce phénomène est dû à l'ionisation des centres F^- qui constituent, pour l'exciton libre, des centres extincteurs efficaces.

Abstract. — The resonant emission observed at 2 125 Å in KI irradiated with electrons at very low temperature increases when the crystal is illuminated by infrared light. This phenomenon is due to the ionization of the F^- centres, which are efficient quenching centres for the free excitons.

Recently [1], a new mechanism concerning primary defect formation was introduced, suggesting that the precursor states responsible for their creation are states of the free exciton (F.E.). On the other hand, experiments on KCl have shown it was possible to reach these precursor states by optical pumping in the exciton relaxed state absorption band [2]. In the iodides, and particularly in KI, the free exciton emits a narrow luminescence band labelled resonant emission, the properties of which are well known (see for instance the references given in [3]). This band can be observed under electron irradiation of the crystal, in spite of the fact that most of the created excitons with this kind of excitation are *self-trapped excitons* (STE) due to capture of electrons by self trapped holes (V_k centres). We have studied the influence on the F.E. luminescence of an additional irradiation of the sample during the electron irradiation. This second irradiation was made with a light of wavelength in the STE main absorption band region [4] which, following ref. [1] could induce an increase in the F.E. emission due to an STE → F.E. transition. For the resonant emission observation, we use the experimental procedure described in ref. [3]. The instantaneous electron energy deposition rate is 10^{22} eV/cm^{-3} s^{-1}. The pumping source is initially a 1 W YAG : Nd Laser, the 1.06 μ emission of which is well adapted for the exciton absorption band in KI [4]. Then, we observe that, when the crystal is under I.R. stimulation during the electronic excitation, the resonant luminescence signal I_R increases by ΔI_R. This quantity can be, following the conditions, of the order of magnitude of the initial signal. ΔI_R persists unchanged during the optical stimulation. The increase and decrease of ΔI_R at the beginning and end of the stimulation are faster than the time constant of the apparatus (100 ms), which agrees with an electronic effect. However the following results show unambiguously that the observed effect is not due to the STE → F.E. transition, but to the influence of the stimulation on the centres created by the irradiation, in spite of the fact that the defect creation rate in KI near liquid helium temperature is very low : (*a*) the resonant luminescence changes with irradiation time : it decreases with dose, whereas ΔI_R increases (Fig. 1) : ΔI_R is about zero with small doses, increases with the irradiation time to a certain limit. This effect is independent of the origin of the studied crystals (Crystal Growth Laboratory Salt Lake City; Laboratoire de Physique Cristalline, Orsay), and is also, roughly, independent of impurity content; (*b*) ΔI_R for determined conditions, depends on the stimulation intensity but a saturation can be reached for a given intensity of the stimulation light; (*c*) By using a light source of 150 W followed by a Bausch and Lomb monochro-

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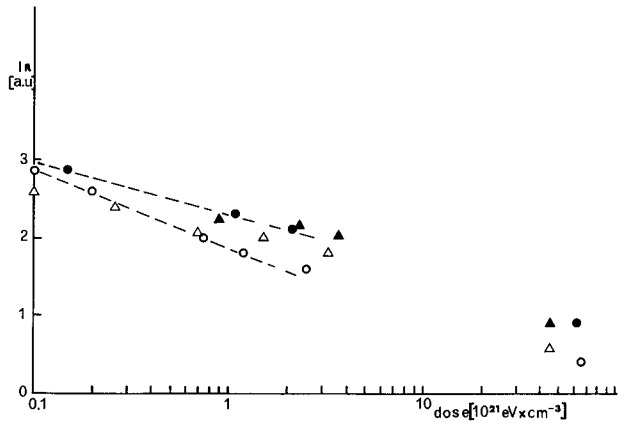

Fig. 1. — Free exciton luminescence intensity, excited by a pulsed electron source, with (●, ▲) and without (○, △) additional light stimulation (see text). The results are displayed for 2 samples : a ultra pure KI (○, ●) and a Li-doped (10 ppm) KI (▲, △). Electron voltage : 30 kV ; Average current ≃ 0.1 μA × cm^{-2} ; Repetition state : 600 Hz ; Light source : 90 W xenon lamp + « MTO J 721 a » filter.

mator, we observe that the stimulation spectrum consists of a large band which is relatively flat between 650 and 1 300 nm with a maximum at about 700 nm which corresponds also to the range of the F^- centres absorption [5]; (*d*) The effect disappears by heating the irradiated sample to 200 K where the F^- centres become thermally ionized [6] : after irradiation at 10 K the crystal is heated to a temperature T, then cooled down to 10 K. Then we record the luminescence signal with and without the optical stimulation. We observe that the I_R intensity is more important after the annealing than before and decreases very rapidly to almost reach its level before annealing. Moreover, ΔI_R is negligible at the beginning of the irradiation and increases rapidly during it. An annealing at a lower temperature than 200 K has no noticeable effect; (*e*) The defect concentration measured by the resonant luminescence quenching for a fixed irradiation dose is the same, whether the sample is optically stimulated or not during the irradiation.

It is well known that the defects created by irradiation lead to resonant luminescence quenching [3]. Our results are well explained if we consider that the electronic transformation of a certain type of quenching centre brings about a decrease of this quenching effect, and also an increase of the signal I_R. It appears that the F^- centres are involved. F^- centres are created in KI by irradiation at very low temperature [7]. They are very easily ionized by optical stimulation, the excited states being located in the conduction band [5]. No other simple defects (H, V_k, F, F^+) have an absorption band corresponding to the stimulation spectrum range. Finally, the optical and thermal ionizations involve the F centre formation, the quenching effect of which for the exciton is known to be weak [8]. Then, if the interaction diameter R with free excitons is more important for F^- than for F centres, the transformation $F^- \rightarrow F$ leads to an increase of the resonant emission. We can note the fact that an annealing at 120 K, where the V_k centres are mobile [6], does not cause any variation concerning the stimulation effect. This indicates a negligible quantity of V_k centres, according to [9] but not to [7]. The charge compensation of F^- centres is probably due to the F^+ centres present in the crystal. Under irradiation, an equilibrium also exists between F, F^+ and F^- centres following $2\,F \rightleftarrows F^+ + F^-$. A sufficiently high I.R. stimulation brings about the ionization of all F^- centres. Nevertheless, we are not able to separate the F^- centre quenching role from that due to F^+, but we can assume that the number of F^- centres, and also of F^+ centres, saturates with the dose. For a given irradiation dose, we have a certain number of vacancies and interstitials. Each type of centre has a capture cross section for the diffusing free exciton. We can write [10] :

$$I_R = \frac{K}{\sum_1 \frac{1}{\tau} + 4\pi D\left(\sum_j n_j R_j + nR\right)}$$

τ_i : time constant for all processes concerning free exciton except the diffusion process,
D : diffusion coefficient of the free exciton,
n_j : population of centres labelled j (except F^- centres and F^+ centres),
R_j : interaction diameter of the centre labelled j with free exciton,
n, R : population and interaction diameter with free exciton of charged vacancies,
K : constant.

When the light stimulation induce $F^- \rightarrow F$ transformations, if we assume the quenching effect of the F centre to be negligible we have :

$$\frac{\Delta I_R}{I_R} \propto -\Delta n\,.$$

Thus the observed effect is proportional to the number of F^- centres bleached in the sample. Then $\Delta I_R / I_R$ increases with the dose of irradiation as more defects, such F^- centres, are present in the crystal (Fig. 1).

To conclude, it was not possible to demonstrate free-exciton formation by optical stimulation observing an effect in the resonant emission. In fact, the sensitivity of the free exciton to the defects is so large that for a very low concentration of defects, lower than 10^{16} cm^{-3}, the resonant emission depends strongly on their presence. The study of the F.E. emission under optical pumping in the near infrared region has shown the existence of a strong interaction between the F.E. and a charged vacancy such as the F^- centre.

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