MAGNETIC EFFECTS OF TUNNELLING RECOMBINATION LUMINESCENCE IN CsI AND KCl DOPED CRYSTAL

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Résumé. — Des cristaux de CsI et KCl dopés avec des impuretés monovalentes telles que Ag, Tl, Na, etc... et exposés à basse température à des radiations ionisantes présentent une luminescence qui persiste plusieurs heures après la fin de l'irradiation. Le processus est interprété comme une recombinaison due à un transfert d'énergie par effet tunnel entre électrons et trous piégés sur des sites voisins. L'application d'un champ magnétique extérieur ($0 \leqslant B \leqslant 6$T) induit dans CsI : NaI et KCl : AgCl (ou : NaCl) une forte diminution de l'intensité de la phosphorescence due à une polarisation partielle des spins électroniques des défauts. Aucun effet n'est observé dans CsI : TlI et KCl : TlCl (ou : CuCl). L'application d'un champ microonde résonant tend à compenser l'effet du champ magnétique et permet dans CsI : NaI seulement, la détection optique de la R. P. E. du centre du type trou self-trappé responsable du processus de phosphorescence.

Abstract. — CsI and KCl crystals doped with monovalent impurities such as Ag, Tl, Na, etc... and exposed to ionising radiations at low temperature present a luminescence which persists many hours after the end of the irradiation. The process is attributed to a tunnelling recombination between nearby trapped electrons and holes. An external magnetic field ($0 \leqslant B \leqslant 6$T) induces in CsI : NaI and KCl : AgCl (or : NaCl) a strong reduction of the intensity of the phosphorescence caused by a partial polarization of the electron spins of the defect pairs. No effect has been found in CsI : TlI and KCl : TlCl (or : CuCl). The application of a resonant microwave field tends to compensate the magnetic field effect and allows in CsI : NaI only, the optical detection of EPR of the hole type defect responsible for the afterglow process.

1. **Introduction.** — It is now well established that exposure of alkali halide crystals doped with impurities such as Tl^+, Ag^+ etc... to ionizing radiation at low temperature results in the trapping of holes as X_2^- centers (V_k centers) and of electrons as Tl^0, Ag^0 and other electronic defects. These crystals emit a luminescence which persists for a long time after the irradiation ; it has been attributed to a tunnelling recombination of electrons with holes trapped on nearby sites (M^0-V_k centers). This phenomenon was first observed in alkali halide crystals by Delbecq *et al.* [1, 2] and later investigated by several authors [3, 4, 5, 6]. It has also been observed in other ionic crystals such as $SrCl_2$ doped with alkali cations [7]. Models for the afterglow kinetics have been worked out [4, 8] using a probability for the radiative tunnelling recombination given as a function of the distance r between the nearby V_k-M^0 defects of the form

$$W(r) = W_0 \exp(-2\alpha r) \qquad (1)$$

It explains satisfactorily the t^{-1} dependence of the afterglow decay time found in alkali halide crystals [4, 5]. Recently Delbecq and Yuster investigated in KCl : AgCl the change in intensity of the afterglow luminescence caused by polarization by a magnetic field of the unpaired electrons spins of Ag^0 and Cl_2^- defects. They observed a strong reduction of the luminescence intensity showing that the final state after the tunnelling process was mainly reached through a singlet state [9].

In this paper we present in section 3.1 results of the magnetic field effect on the decay kinetics of the phosphorescence performed mainly with CsI doped with NaI and TlI. Some preliminary measurements with KCl doped with AgCl, CuCl, NaCl and TlCl will also be shown. In section 3.2 we report on low field effects and optical detection of EPR performed for the first time in CsI : NaI. We study just those pairs involved in the tunnelling recombination process contrary to conventional EPR experiments which measure all the defects present in the crystal. Tentative interpretation of our results is finally given in section 4.

2. **Experimental procedure.** — Several single crystals doped with different impurities were used for these experiments : CsI : NaI, CsI : TlI, KCl : CuCl, KCl : TlCl, KCl : AgCl [1], KCl : NaCl [1]. They were irradiated at LHeT with typically 150 kV, 10 mA

[1] We thank Prof. J. P. Chapelle (Orsay) and Prof. F. Lüty (Salt Lake City) for kindly supplying these crystals.

X rays from a Mueller MG 150 tube with a tungsten target.

In the magneto-optic experiments the sample ($10 \times 5 \times 1$ mm^3) was placed in the exchange gas cell of a superconducting splitcoil cryostat having optical access in the four horizontal positions (Spectromag SM4, Oxford Instruments). The magnetic field could be varied from 0 to 6T. The temperature used for these experiments was $1.4 < T < 4.2$ K. The luminescence propagating along or perpendicular to the field was gathered by a lens placed inside the cryostat and then with a series of lenses brought to EMI 9558 QB photomultipliers. The tubes were especially well shielded and placed at about 1 meter from the magnet to prevent a direct effect due to the magnetic field. After detection the signals were fed into a Keithley 414S or 410 picoammeter and then sent to a multipen strip chart recorder. When necessary different interference or broad band optical filters and Polaroid sheet polarizers were placed in front of the PMT.

In the low field and optical detection EPR experiments the sample ($8 \times 4 \times 2$ mm^3) was placed on its longest side on the bottom of a cylindrical copper cavity excited in its TE_{111} mode. Three windows allowed irradiation, infrared stimulation and detection of the phosphorescence (with a well shielded photomultiplier EMI 9558 QB) either parallel or perpendicular to the static magnetic field. X-band microwaves were chopped with PIN diodes. The optical signal was amplified selectively and phase detected with a PAR 124 A lock-in amplifier. For transient measurements, the signal to noise ratio was improved by means of a signal averager (HP 5480 A). All the measurements have been performed at 4.2 K.

3. **Experimental Results.** — 3.1 EFFECT OF A STRONG MAGNETIC FIELD. — Delbecq *et al.* [9] have recently observed that the intensity of the phosphorescence in KCl : AgCl decreased when the sample was placed in a magnetic field ($B_{max} = 3.2$ T). We have extended the range of the parameter B/T and tested his model for KCl : AgCl and (: TlCl), (: NaCl), (: CuCl) and for CsI : NaI and (: TlI).

Figure 1 shows for all KCl crystals the relative change $\Delta I/I_0(B = 0)$ of the phosphorescence intensity plotted as a function of B/T [T/K]. The temperature has been varied from 4.2 down to 1.4 K and the magnetic field from 0 to 5.7 T. The solid and dotted lines are calculated. It is interesting to see that no change has been observed with TlCl and CuCl doping (curve e) and that our results for AgCl doping (curve b) are in relatively good agreement with those of Delbecq *et al.* (curve a) who measured the effect for the range $0 < B/T < 2.2$ only.

Figure 2 shows our results for CsI : NaI and (: TlI). Again no effect is found for TlI doping (curve b) but an important change occurs for CsI : NaI although the saturation value of $\Delta I/I_0$ is smaller than in KCl : AgCl.

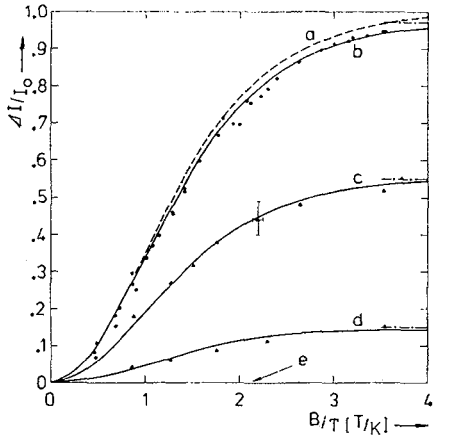

FIG. 1. — Relative change $\Delta I/I_0$ of the phosphorescence as a function of B/T. The solid curves are fitted according to eq. (8) (see also text) : *a*) Theoretical curve taken from Delbecq's results for KCl : AgCl [9] ; *b*) KCl : AgCl X-irradiated at LHeT ; *c*) KCl : NaCl X-irradiated at LHeT ; *d*) KCl : NaCl X-irradiated at LNT ; *e*) KCl : CuCl and (: TlCl) X-irradiated at LHeT (no effect).

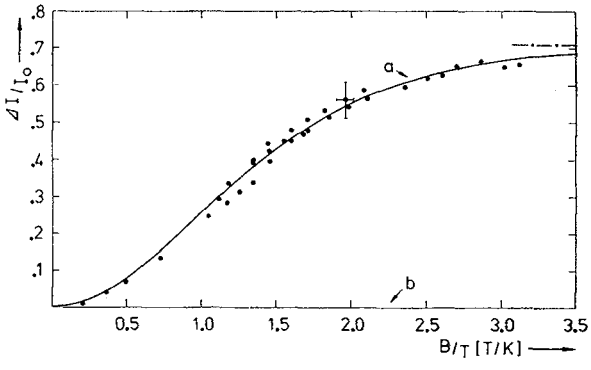

FIG. 2. — Relative change $\Delta I/I_0$ of the phosphorescence as a function of B/T. The solid curve is fitted according to eq. (8) (see also text) : *a*) CsI : NaI ; *b*) CsI : TlI (no effect).

Decay time measurements under magnetic field are governed by the same law which described the process without applied magnetic field [5] :

$$I(t) = Ct_0^{-1} \ln (1 + t_0/t) . \qquad (2)$$

Therefore neither the average tunnelling probability $W(r)$ (eq. (1)) nor the luminescence efficiency are affected by the magnetic field. However the hypothesis of Delbecq *et al.* [9] that the tunnelling process is permitted if and only if the electron spins of the $(V_k - M^0)$ pair are antiparallel is not justified.

We assume in first approximation that the recombination may occur via singlet and triplet state with different probability $W_s(r)$ and $W_t(r)$ independant of the magnetic field. We define

$$A = \frac{W_t(r)}{W_s(r)} \qquad (3)$$

and N_i the relative population of the four energy levels of the pair [10] such that $\sum_{i=1}^{4} N_i = 1$

$$E_{1,4} = \pm \tfrac{1}{2}(g_1 + g_2)\,\mu_B\,B$$
$$E_{2,3} = \pm \tfrac{1}{2}(g_1 - g_2)\,\mu_B\,B \qquad (4)$$

where g_1 and g_2 are the g factors of the M^0 and V_k centers (assumed for the moment isotropic for simplicity).

If the orientation of the unpaired electron spins of any pair are independent we can apply the Boltzmann statistics. The intensity of the phosphorescence is then given as a function of B and T by

$$I(t\,;\,B,\,T) = \alpha(B,\,T)\sum_j N(r_j,\,t)\,W_s(r_j) \qquad (5)$$

with $N(r_j, t)$ being the number of pairs having a separation r_j at time t while

$$\alpha(B,\,T) = N_2 + N_3 + A(N_1 + N_4) \qquad (6)$$

is the fraction of pairs allowed to recombine by tunnelling. Note that

$$\alpha(B = 0,\,T) = \alpha_0(T) = \tfrac{1}{2}(A + 1).$$

We can easily calculate the relative population N_i in term of

$$Y_i = \exp(g_i\mu_B\,B/kT)$$

to finally get

$$\frac{\Delta I}{I_0} = \frac{I_0(t\,;\,B = 0,\,T) - I(t\,;\,B,\,T)}{I_0(t\,;\,B = 0,\,T)} = 1 - \frac{\alpha(B,\,T)}{\alpha_0(T)}. \qquad (7)$$

In CsI the g factor for Na^0 is not known although we have tried to measure it. It is probably isotropic and its value is certainly near $g_1 = 2$. For the V_k centers the g factors are anisotropic so that the orientation of the defects with regard to the field plays an important role. For CsI we consider that $\frac{2}{3}$ ($\frac{1}{3}$) of the V_k are aligned perpendicular (respectivally parallel) to the field applied along a [100] direction. The g values are $g_2^{\perp} = 2.27$ and $g_3^{\parallel} = 1.89$ [11]. In KCl $g_1(Ag^0)$ equals 1.996 and is isotropic. The V_k centers are aligned along the six [110] directions so that $\frac{2}{3}$ ($\frac{1}{3}$) of the V_k are at 45° (respectivelly parallel) to the field applied along a [100] direction. The g values are : $g_2^{45°} = 2.02$ and $g_3^{\parallel} = 2.04$.

Taking in account this modification we get for both type of crystals

$$\frac{\Delta I}{I_0} = 1 - \frac{4}{3}\frac{(Y_1 + Y_2) + A(Y_1\,Y_2 + 1)}{(1 + Y_1)(1 + Y_2)(1 + A)} - \frac{2}{3}\frac{(Y_1 + Y_3) + A(Y_1\,Y_3 + 1)}{(1 + Y_1)(1 + Y_3)(1 + A)} \qquad (8)$$

This relation is identical to that of Delbecq when $A = 0$.

The dotted and solid lines of figure 1 have been calculated according to this law. Curve a is the result predicted by Delbecq for KCl : AgCl with $A = 0$. Our results (curve b) are better fitted with $A = 0.013$, the limit of $\Delta I/I_0$ for large B/T being 0.974. Curve c fits the results for KCl : NaCl X irradiated at LHeT with $A = 0.29$, $\Delta I/I_0$ max $= 0.55$ while curve d has been obtained after X irradiation at LNT. In this case $A = 0.74$ and $\Delta I/I_0$ max $= 0.15$. The defects involved in this tunnelling process are certainly different since Na^0 centers have never been observed in these crystals. The recombination may occur between F and V_K or V_{KA} centers which all have g values very similar to what we have assumed. Since no effect is observed in KCl : CuCl and (: TlCl) the A values are unity.

Curve a of figure 2 refers to CsI : NaI and is fitted with $A = 0.17$ with a $\Delta I/I_0$ max $= 0.71$. $A = 1$ for CsI : TlI (curve b).

Let us note that in the experiments the magnetic field could not be turned on or off rapidly. It is therefore not possible to calculate the ratio $\Delta I/I_0$ directly from the experimental graphs and the correct I_0 and ΔI were computed. Details will be found in [5].

3.2 EFFECT AT LOW FIELDS ON THE PHOSPHORESCENCE AND OPTICAL DETECTION OF THE PARAMAGNETIC RESONANCE. — A low magnetic field (up to 0.5 T) should decrease the phophorescence intensity, as it is the case at higher fields but the effect due to the Boltzmann factors on the equilibrium populations of the spin states is too small to be measured. However, if the light is observed along the magnetic field, a larger linear effect shows up : when turning on the field the relative change of the phosphorescence amounts to 2.7 % per Tesla (Fig. 3). This behaviour is hidden at high fields by the much stronger Boltzmann effect and cannot be observed in this range. This indicates that another magnetic field dependent mechanism occurs ; it also decreases in first order

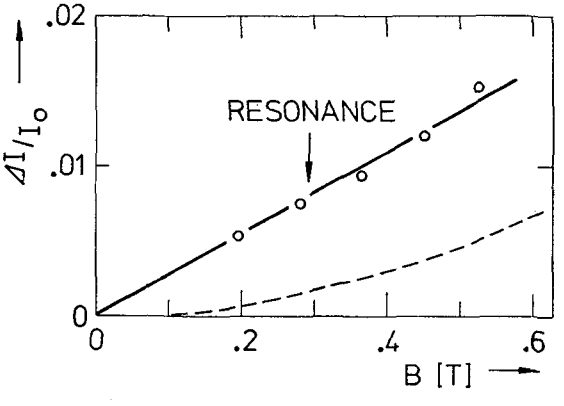

FIG. 3. — Relative change of the phosphorescence intensity due to the magnetic field at 4.2 K for X-irradiated CsI : NaI. Lower line : calculated effect of the Boltzmann factors for two pure triplet and two mixed triplet-singlet states.

perturbation the singlet admixture of some of the spin states, reducing thereby the tunnelling rate ; it is not yet elucidated, but it could be analogous to the one found in F center pairs [10].

Application of resonant microwaves enhances the phosphorescence (OD-EPR). At high microwave power, the light enhancement due to EPR can almost compensate the decrease produced when turning the field on. The magnitude of the effect is stronger with an infrared stimulation of the crystal, which liberates electrons from the traps [5]. The principal emission occurs also at 420 nm, but weak ultraviolet luminescence at 290 nm and 338 nm are present from intrinsic recombination of uncorrelated electrons and V_K centers ; they are not influenced by the EPR. For given IR excitation and microwave power, the EPR signal decreases with time proportionally to the phosphorescence.

The spectrum of the OD-EPR signal depends on the direction of the emitted light. When the luminescence is observed perpendicularly to the magnetic field through linear polarizers one obtains two different spectra, according to the direction of the polarization axis with respect to the magnetic field. They are at the same position and have the same overall features but with much broader lines that those of I_2^- centers observed in CsI : NaI by standard EPR [11]. Figure 4 shows the spectrum obtained with the light polarization parallel to the magnetic field, which corresponds to I_2^- centers having their axis along the field direction. If the luminescence is observed along the field, there is no dichroism, since only I_2^- centers perpendicular to the field are visible. This result shows that the phosphorescence emission is almost completely polarized parallel to the [100] molecular axis of the V_K centers. Although the optically detected centers are probably of I_2^- type, the low resolution prevents to determine eventual perturbations due to the sodium (e. g. V_{KA}).

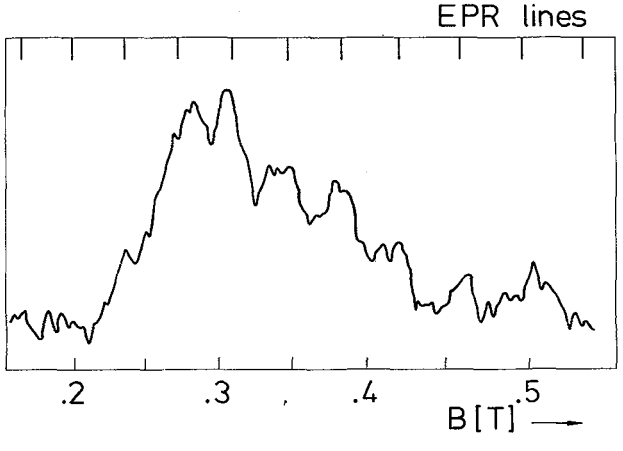

FIG. 4. — Spectrum of optically detected EPR of V_K centers in CsI : NaI (9337 MHz, 4.2 K). Phosphorescence emission perpendicular and polarization parallel to the magnetic field. On the horizontal axis : position of the conventional EPR lines of V_K centers parallel to the field.

If the applied microwave power is increased (up to 100 mW) the signal saturates (Fig. 5), the product of the relaxation times being $T_1 T_2 = 3 \times 10^{-12}$ s^2. A spin-lattice relaxation time of the order of 10^{-3}s would yield a homogeneous broadening of 200 G, of the order of the line width.

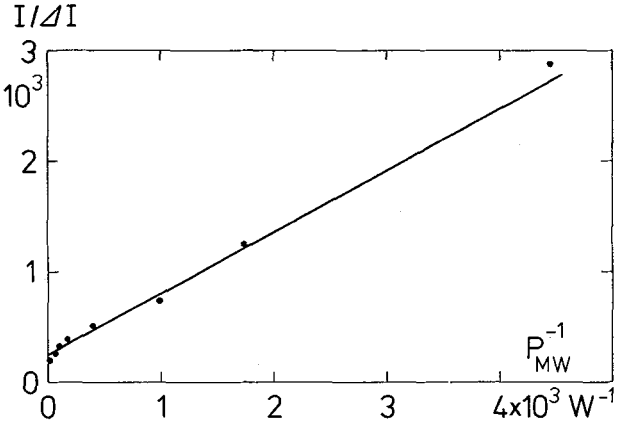

FIG. 5. — Saturation of OD-EPR of V_K centers in CsI : NaI at 4.2 K. The inverse of the signal is plotted versus the inverse of the microwave power.

The transient behaviour of the phosphorescence when the microwaves are turned on and off depends on the power. Figure 6 shows that with pulses of about 3 ms duration, at low power, the signal builds up according nearly to a law : $1 - \exp(-t/t_1)$. At high power it contains two exponentials : $\exp(-t/t_2)$-$\exp(-t/t_3)$. The decay time t_4 is independent of the power.

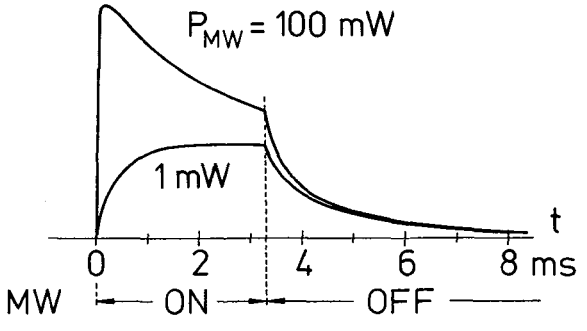

FIG. 6. — Transient behaviour of the OD-EPR signal of V_K centers in CsI : NaI at 4.2 K at high and low microwave power.

This is consistent with a model in which half of the states can be emptied by tunnelling (probability per unit time W) and can be transfered to the other non-tunnelling states either by spin lattice relaxation ($1/T_1$) or by EPR (M), with $1/T_1 \ll W$ and $M \ll$ or $\gg W$, according to the applied power. The relaxation times are found to be : $t_1 \cong W$, $t_2 \cong W/2$, $t_3 \cong 2M$ and $t_4 \cong W$. This corresponds roughly to the measurements, the difference being accounted for by the fact that the parameters are not unique but distributed and that the model is certainly too simple. In

principle we could expect to obtain OD-EPR spectra for crystals which show a decrease of the phosphorescence due to the magnetic field. A search in KCl : AgCl was however unsuccessful. As shown in section 3 KCl : TlCl and CsI : TlI do not show a magnetic field induced change of the phosphorescence ; as expected no OD-EPR spectra have been obtained.

4. **Conclusion.** — The behaviour of the phosphorescence emission under magnetic field leads to some remarks. Up to now only system containing neutral impurities having one ns electron outside closed shell (such as Ag^0 and Na^0) show a quenching of the phosphorescence. The spin polarization of the unpaired electrons by the magnetic field is the dominant mechanism and the final state reached after the electron transfer appears as a mainly singulet state. The different values of the relative variation $\Delta I/I_0$ observed in KCl : AgCl and CsI : NaI are however not yet elucidated. In KCl : NaCl we probably deal with a (V_{KA}-F) centers electron transfer ; however more detailed investigations should be done. In particular studies with KI and KBr doped with Tl^+ ions or NaCl : AgCl which are believed to have electron transfer transition would be interesting in order to test the model further. Attention should also be paid to any low field magnetic quenching which may lead to optical detection of the EPR. This last powerful technique should provide an identification of the defects and of their interaction with their surroundings.

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DISCUSSION

N. ITOH. — Do you have any comments on the distance between the V_k-center and the impurity based on your work on EPR of the composite system ?

C. JACCARD. — The EPR spectra obtained thus far do not show any feature which can be attributed unequivocally to sodium, and therefore do not yield information on the pair separation. From analogous tunnelling phenomena in F-F-pairs, a distance between 1 and 10 nm could be possible.

G. GUILLOT. — Why crystals doped with Thallium have different behaviour ?

C. JACCARD. — In the case of Tl-doping, the hole jumps from the V_K-center to the filled 6s-shell of Tl^0. This can be done independently of its spin, and therefore this process is not affected by a strong magnetic field. In the case of Na-doping, the single 3s-electron of Na^0 jumps into the V_K-center. For this it must have the right spin, and a strong magnetic field reduces the transfer rate.