

Cathodoluminescence of KCl Single Crystals at Room Temperature

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This is a study of the cathodoluminescence of KCl single crystals with an electron probe working in a very high vacuum. A kinetic analysis shows a close relation between this cathodoluminescence and the evolution of the crystal under irradiation, i.e., the density of the colour centres created. In particular, two processes are seen to cause the decrease in luminescence: self-absorption and quenching, as a function of centre concentration.

La cathodoluminescence de monocristaux de KCl a été étudiée à l'aide d'une sonde fonctionnant en ultra-vide. L'analyse de sa cinétique montre l'étroite relation de celle-ci avec l'évolution du cristal sous irradiation, c'est-à-dire la densité des centres colorés créés. En particulier, nous avons mis en évidence deux processus concourant à la décroissance de la luminescence: l'auto-absorption et l'extinction en fonction de la concentration en centres.

An observation of alkali halide crystals with a scanning electron microscope has enabled us to witness an evolution of cathodoluminescence during irradiation (1). In order to make a quantitative study of this phenomenon we erected an electron probe (2). The results obtained for KCl are summed up in this paper.

Experimental

The irradiation conditions (i.e., the domain of our study) are as follows: spot diameter 5 mm; V , energy, between 15 and 50 kV; d , irradiation density, between 0.5 and 15 $\mu\text{A}/\text{cm}^2$. The samples are kept away from any sort of light radiation during the experiment.

The KCl samples are nondoped, and are of various origins [Korth (Germany), Quartz et Silice (France)] and of varying quality (P.A. or ultrapure crystals¹). They are cleaved to form slices of $8 \times 8 \times 0.5$ mm. To avoid charge effects when they are irradiated, one side is covered with aluminium and connected to the sample holder. The thickness of the layer (about 100 Å) and thus its reflection power vary from one vaporization to another, but do not noticeably affect the electron beam (3). Except for

¹ Korth specification—P.A: pro analysis. Material for special optics. Ultrapure: the impurity content ranges from 10^{-4} to $10^{-6}\%$.

some particular cases, each series of experiments (i.e., the study of 10 successive crystals contained by the sample holder) is realized with samples vaporized together.

To compare the different series, we record, for each of them, a reference curve with the help of a sample irradiated at 30 kV with an electron density of 1 $\mu\text{A}/\text{cm}^2$.

An optical device placed under the sample holder is used to observe, through a window, the cathodoluminescence transmitted by the lower surface of the sample (which is not covered with aluminium). The detection system consists of an XP 1002 Radio-technique photomultiplier, fitted, if required with filters, and of an Electronik 19 Honeywell recorder.

Results

Description of the Kinetic Curve

We measure the whole of the light intensity emitted between 3500 and 7500 Å (range of the photomultiplier's photocathode sensitivity).

The kinetic curves of cathodoluminescence obtained in unvarying irradiation conditions with samples of different qualities and origins are identical. As the dispersion of the measurements is not higher than for a set of samples obtained from one single crystal, we can safely say that we are confronted with an intrinsic phenomenon of KCl.

It should be added that, although for high irradiation energy the temperature at the surface of the sample may be a few degrees higher, no bleaching or other thermal effect is observed. In fact the kinetic curves obtained with continuous irradiation are exactly like those obtained in successive parts with intermittent irradiation.

All the recorded curves have the same shape as the α experimental curve on our diagram.

These curves may be analysed in three sections.

Section I does not last more than 0.5 sec and is distinguished from Section II only in high speed recordings or when irradiation is of very low electron density. We shall only describe and interpret it qualitatively.

Section II: Cathodoluminescence reaches a maximum value M , depending on the conditions of irradiation. Its duration, T_m , varies from a few seconds to 100 sec.

If, for a given energy, we plot I/d vs $t \times d$ (I : luminescence intensity) on the same diagram for various values of d , we always get curves that can be roughly superposed.

For a fixed density, the maximum value increases

with V in a quasilinear way, and T_m also increases (by 50% for $d = 5 \mu\text{A}/\text{cm}^2$).

Section III. After M , the luminescence decreases slowly down to an asymptotic value. (Its variations can still be detected for more than one hour.)

Interpretation

We think there is a close relationship between cathodoluminescence and colour centre formation.

We believe that Section I corresponds to the early stage of coloration, observed on all the growth curves of F centres in KCl (4) and that its amplitude depends on d and on the number of initial defects.

In Sections II and III, both the increase and the decrease in luminescence are related to the evolution of the density of the centres. This hypothesis is based on the results concerning Section II described above, and on an analysis of the function representing the kinetic curve of Section III, from a time value slightly higher than T_m .

This function,

$$\exp - K \left(1 - \frac{1}{\sqrt{bt + 1}} \right),$$

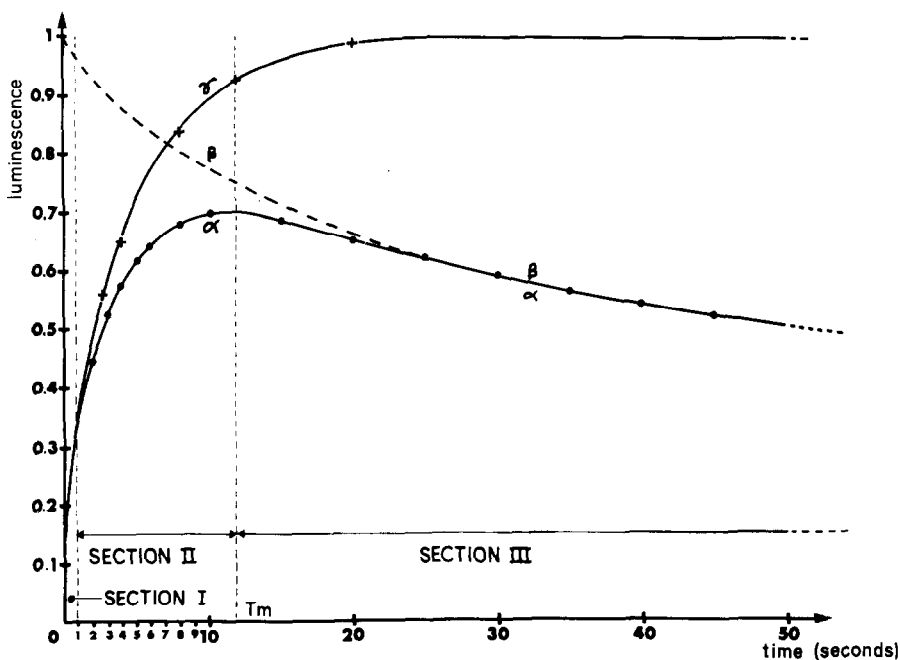


FIG. 1. Example of kinetic curve of KCl cathodoluminescence at room temperature.

α : experimental curve. Recording made with a P.A. KCl single crystal irradiated with 30 kV, $10 \mu\text{A}/\text{cm}^2$

β : theoretical curve $\exp - K \left(1 - \frac{1}{\sqrt{bt + 1}} \right)$. The parameters $K = 1.7$ and $b = 4 \times 10^{-2} (\text{sec}^{-1})$ are computed with experimental data, using the least-squares method (applied to the loglog of $I(t)$)

γ : corrected curve.

(see β curve in the figure) is in fact the same as that representing the variations of light transmission at the F -band maximum through a KCl crystal under the same irradiation conditions (5), except for the value of K . b is of the same order of magnitude in both types of experiment according to: $b \sim d$, for V fixed, and $b \sim V^{-1/2}$, for d fixed (6).

A study of the variations of the parameter K with V shows, however, that the decrease in luminescence recorded cannot be imputed merely to the absorption of the emitted light by the colour centres (self-absorption), particularly as the value of K is too high when V is low. This is confirmed by a study of the spectral kinetic curves of the cathodoluminescence. We recorded the kinetic curves in domains of precisely determined wavelengths, and compared them with those obtained in optical absorption, under the same experimental conditions. In luminescence, the parameter K retains a nonvanishing value in the range where optical absorption, and thus self-absorption, is negligible, and consequently shows the decrease in luminescence to be intrinsic. This study enables us to find out the relative parts played by the two processes in the decrease of the light emitted: self-absorption and quenching effect, which is a function of concentration and has the same variation law as a function of time.

For 30 kV, $2 \mu\text{A}/\text{cm}^2$, we deduced that quenching is about 30% responsible for the total decrease in luminescence. Below 30 kV, this process becomes preponderant, whereas above, the decrease in luminescence is due mainly to self-absorption. Furthermore, an increase in electron density stimulates both phenomena simultaneously.

By computing b and K , for each recording, we can

eliminate the influence of both effects and obtain an idealized kinetic curve (see γ curve in Fig. 1).

Conclusion

The study of KCl cathodoluminescence at room temperature and the knowledge of the laws of growth curves of colour centres in electron irradiated crystals (5, 7, 8) show that

(1) Cathodoluminescence (idealized curve) reaches saturation for concentrations of colour centres (F and V) that are roughly constant and are of the order of 20% of those obtained under prolonged electron irradiation.

(2) This saturation value is proportional to the density of the electron beam.

(3) The decrease in luminescence is due to two phenomena: (i) the self-absorption of the light by the F centres created; (ii) the intrinsic quenching which we interpret by a decrease in the yield of luminescence centres as a function of the concentration of F or V centres.

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