

# LUMINESCENCE AND ABSORPTION SPECTRA OF NaF SINGLE CRYSTALS \*

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The radiative electron-hole recombination of crystals subjected to  $X$ -ray irradiation has often been studied in alkali halides, but no correlation has been found between emission intensity and absorption coefficient of any known colour center. This is possibly due to the fact that in the most extensively studied salts the well-known luminescence of  $F$ ,  $M$  and  $Z$  centres falls in a spectral range where the detection is rather difficult. In order to avoid this difficulty, we have reconsidered the problem in NaF single crystals, where the  $F$  and  $M$  luminescence bands lie in the visible or near infrared. At  $80^\circ\text{K}$  a fast growth of the  $F$  band appears, centred at  $3385\text{ \AA}$ , which does not show saturation, while at room temperature there is a definite growth of a band centred at  $5050\text{ \AA}$ , which is usually assigned to the  $M$  centre. The study of the absorption and emission spectra, as a function of the  $X$ -ray dose absorbed by the crystal, has shown a correlation between the  $M$  band absorption and an emission band centred at  $6700\text{ \AA}$ ; the same emission is obtained by photostimulation in the  $M$  band, and, with a lower yield, by photostimulation in the  $F$  band. A possible mechanism responsible for the above described behaviour is suggested. Results on thermoluminescence curves are also reported.

## 1. Introduction and problem

Sodium fluoride is one of the few alkali halides which has received relatively little consideration in research on colour centres and the luminescence of simple solids. No paper, as far as we are aware, has been published for some twenty years the early work of Barth and Lunde on the coloration of natural NaF [1], and of the Göttingen School (Ottner, Mollwo and Molnar, see ref. [2]). The position of the  $F$ ,  $R$  and  $M$  band maximum was found to agree reasonably with the empirical formula proposed by Ivey [2, 3].

It is very possible that this lack of interest in the properties of colour centres in NaF is due to practical reasons: single crystals of sodium fluoride

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are not as easy to grow as *e.g.* KCl; KBr or NaCl; moreover additive coloration seems to be very difficult to obtain, if altogether possible (see *e.g.* the recent attempts with LiF [4], which is in many respects similar to NaF).

More recently, new interest arose in connection with the development of the techniques of ESR and ENDOR [5].

In addition to those on magnetic resonance, we should mention several other papers: the results of Rabin and Klick [6] on the energy necessary for creating *F* centres at helium temperature by ionizing radiation, supporting the idea that *F* and *M* centres are created in pairs by some Varley-type mechanism; the work of Sharma on thermoluminescence [7]; of Bohun [8] on electroemission and thermoluminescence above RT; and of Feofilov [9] on photoluminescence.

Bohun found that maximum thermal bleaching of the *F* band is at 337°C, and that the thermal depth of *F* centres is 0.4 eV; moreover, he located an external electron emission due to the optical excitation of *F* centres. Feofilov studied stimulation spectra and found the same emission by stimulating either the *F* or the *M* band.

It may be that we overlooked other contributions, because of the difficulty of reading articles [10] in Russian.

We think it is worth while to reconsider the properties of sodium fluoride more systematically; we have therefore studied photo and thermoluminescence in *X*-irradiated samples, emission spectra under *X*-ray irradiation and colour centre growth curves.

The main aim of our research is to study possible electron-hole recombination at the *F* centres or, eventually, *F* emission during creation of the centres. Radiative electron-hole recombination in crystals subjected to *X*-ray irradiation has often been studied in alkali halides but no correlation has been found between the emission intensity and absorption coefficient of any known colour centre. This may be due to the fact that in the most extensively studied salts the well-known luminescence of *F*, *M* and *Z* centres falls in a spectral range where detection is rather difficult. In this respect NaF is a suitable material because the *F* and *M* luminescence bands lie in the visible or nearest infrared.

## 2. Experimental methods

The NaF single crystals used in this work were cleaved from batches furnished by the Harshaw Chemical Company, and by Dr. Korth of Kiel.

Optical absorption measurements were performed at liquid nitrogen temperature, with a Cary 14 recording spectrophotometer equipped with a metal cryostat. Samples were *X*-irradiated at 6 cm with a Machlett OEG50 high-intensity source operated at 50 kV and 40 mA; the *X*-ray beam was filtered through a polythen window 0.3 mm thick, in order to ensure more

uniform absorption. The absorption spectra were adjusted for the background of the non-irradiated crystal.

The apparatus for luminescence is described elsewhere<sup>1</sup>; optical excitation was achieved with a 1000 W Hanovia hydrogen discharge tube model 471 A 0320, in the wavelength range from 2000 Å to 3300 Å, and from 3300 to infrared with a 1000 W Wolfram lamp.

### 3. Experimental results

3.1. Growth of the absorption band. Typical absorption spectra, obtained on samples from different sources, are shown in Fig. 1. *F* and *M* bands have the absorption maximum located at  $\lambda_F = 338 \text{ m}\mu$  (3.70 eV),

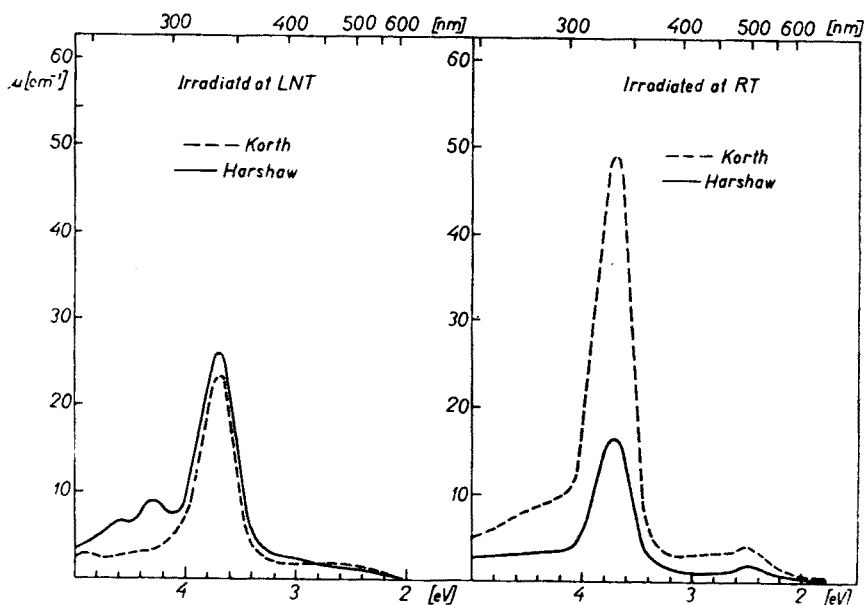


Fig. 1. Typical absorption spectra obtained on samples from different sources irradiated at RT and at LNT

$\lambda_M = 500 \text{ m}\mu$  (2.47 eV) at LNT, in agreement with earlier data; the coloration is much more prominent in Korth's crystals than in those from Harshaw: we shall often have occasion to notice, also in the photo, radio and thermoluminescence properties, that samples of various origin show remarkably divergent behaviour.

<sup>1</sup> R. Fieschi, E. Panizza and P. Scaramelli -- this conference.

When  $X$ -irradiation is performed at LNT two other bands show in the  $u.v.$  at  $\lambda \simeq 270 \text{ m}\mu$  and  $\lambda \simeq 289 \text{ m}\mu$  and a large band at  $460 \text{ m}\mu$ . No  $M$  absorption is detected.

Heating the sample up to RT yields complete bleaching of the 270 and 290  $\text{m}\mu$  absorption bands, and a strong decrease in the  $F$ ; it therefore seems likely that the two high energy bands are due to  $V$ -type centres. After further heating to  $373^\circ\text{K}$  the  $F$  band decreases slightly and the absorption between 380 and  $480 \text{ m}\mu$  disappears.

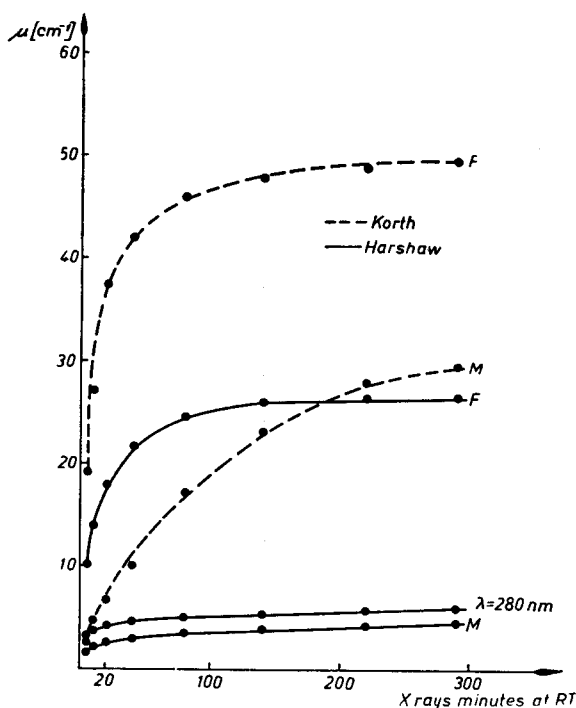


Fig. 2. Growth curves for the absorption coefficient of  $F$  and  $M$  bands,  $X$ -irradiated at RT

Under  $X$ -irradiation at room temperature the induced  $u.v.$  absorption is weaker and ill resolved; at a high dose of irradiation a new absorption at  $462 \text{ m}\mu$  appears.

The growth curves for the  $F$  and  $M$  bands are summarized in Figs 2 and 3.

3.2. Photoluminescence and excitation spectra. When the sample previously irradiated at RT is stimulated at LNT in  $F$  band absorption, an emission band appears with maximum located at  $661 \text{ m}\mu$ ; another one, very weak and unresolved, has its maximum at about  $785 \text{ m}\mu$ . When it is stimulated in  $M$  band absorption, only a strong  $661 \text{ m}\mu$  emission band appears (Fig. 4). This emission had been detected by Feofilov [9], who already remarked

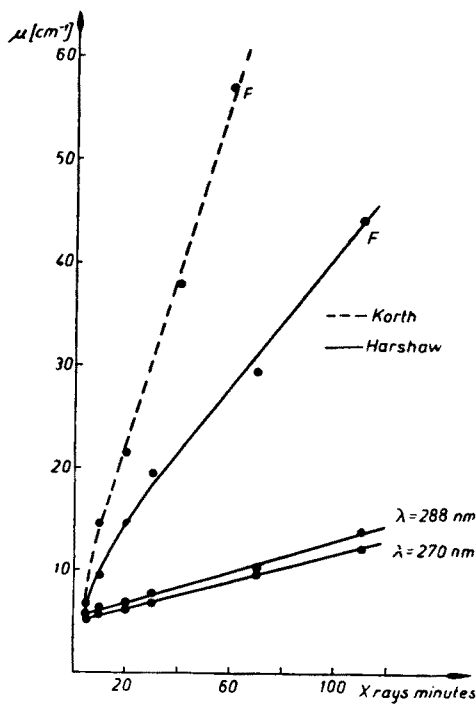


Fig. 3. Growth curves for the absorption coefficient of  $F$  and other  $u. v.$  bands,  $X$ -irradiated at LNT

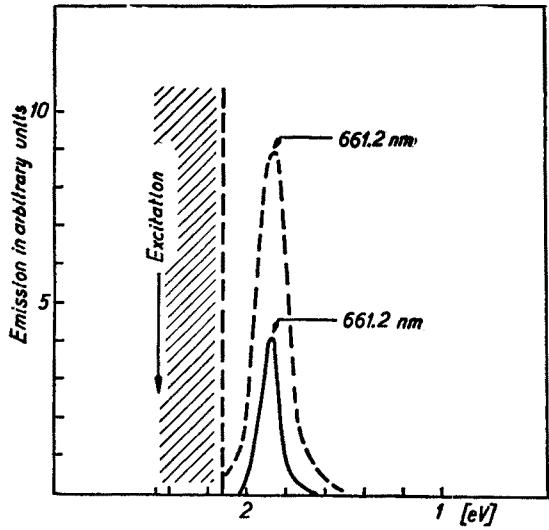


Fig. 4. Sample previously  $X$ -rayed at RT; 661.2  $m\mu$  emission, optically stimulated at LNT:  
 --- incident light at 500  $m\mu$ ; — at 338  $m\mu$

that the same emission occurs at the two different excitation wavelengths. Optical stimulation at RT yields only very weak emission.

The 661 m $\mu$  emission intensity stimulated, with very narrow slits at the monochromator, by light at different positions of the *M* band absorption, is proportional to the absorption coefficient of the *M* band at these wavelengths (Fig. 5).

The emission at 785 m $\mu$  may be due to the *F* band. It is known, however, that in other alkali halides interaction of *F* and *M* centres gives complicated resonance and quenching effects.

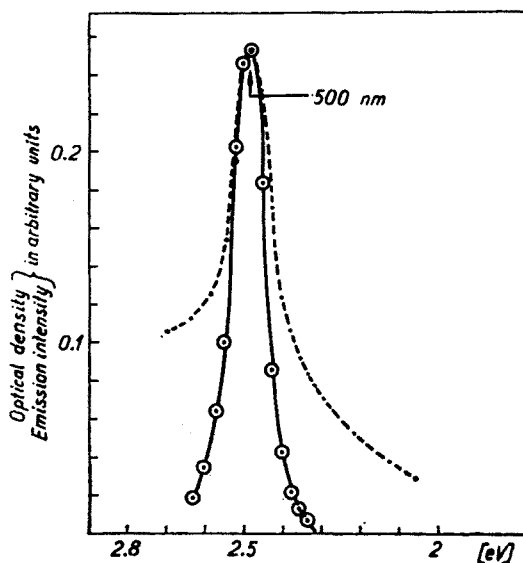


Fig. 5. L. N. T. emission at  $\lambda = 661 \text{ m}\mu$ , stimulated by light of different wavelength in the *M* band absorptions, compared with the optical density. In abscissa the wavelength of stimulating light. ● — absorption, ○ — emission

Stimulation spectra show that the 661 m $\mu$  emission is strongly excited by incident light at 500 m $\mu$  (*M* band); a much weaker emission is detected also under excitation in the *F* band. This might be due to the fact that the *M* centres have a second absorption concealed under the *F* bands, as in other alkali halides.

3.3. Emission spectra under *X*-ray irradiation. Fig. 6 shows a typical emission spectrum of an NaF Harshaw crystal as induced by *X*-rays at room temperature. In identical conditions, the emission spectra of Korth NaF crystals do not show the little bands in the violet and ultraviolet ranges, that decrease in the Harshaw crystals during irradiation.

The growth curve of the 661 m $\mu$  emission band plotted in Fig. 7 is roughly proportional to the intensity of *M* absorption (Fig. 2). This result and the results shown in Fig. 5 (discussed in 3.2 point to the 661 m $\mu$  band as *M* emission).

A new emission band centred at about  $990\text{ m}\mu$  appears after long  $X$ -ray irradiation, increasing linearly.

At LNT only one emission band appears at  $\sim 785\text{ m}\mu$ ; its growth curve is shown in Fig. 8.

Notice the different behaviour of  $785\text{ m}\mu$  in Korth and Harshaw crystals.

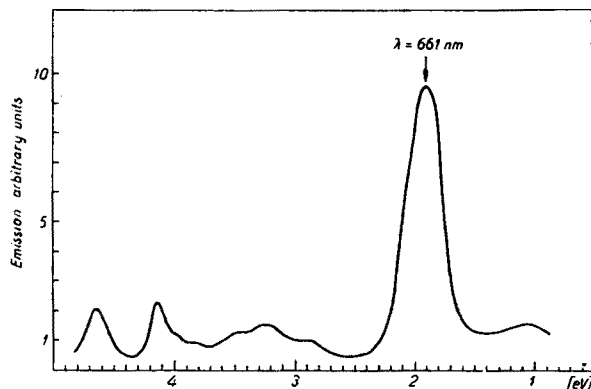


Fig. 6. Emission spectrum by  $X$ -rays in Harshaw NaF at RT

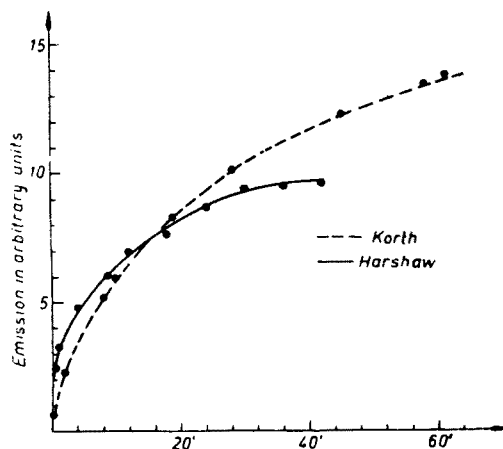


Fig. 7. Growth curve of emission at  $661\text{ m}\mu$  induced by  $X$ -rays at RT

**3.4. Thermoluminescence.** Glow curves of crystals  $X$ -irradiated at LNT have been previously reported by Sharma, who found a well-defined peak at  $174^\circ\text{K}$ , followed by overlapping peaks at  $316^\circ\text{K}$  and  $370^\circ\text{K}$ . Our results for three different samples are shown in Fig. 9, where resemblance with the previous results of Sharma is only vague; this might be due to the higher dose received by our samples: as known, the dependence of the various peaks on the dose is not uniform [11].

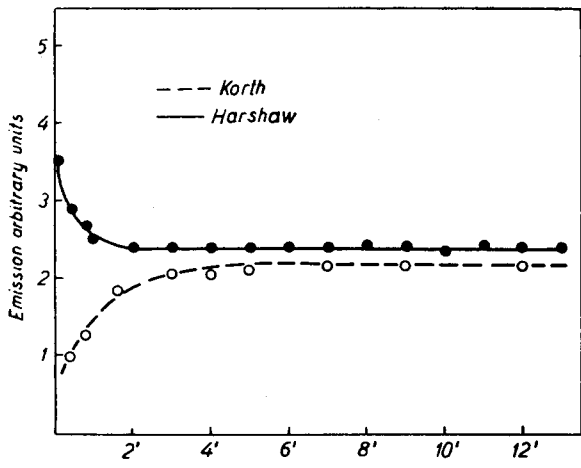


Fig. 8. Growth curve of emission at 785 mμ induced by X-rays at LNT

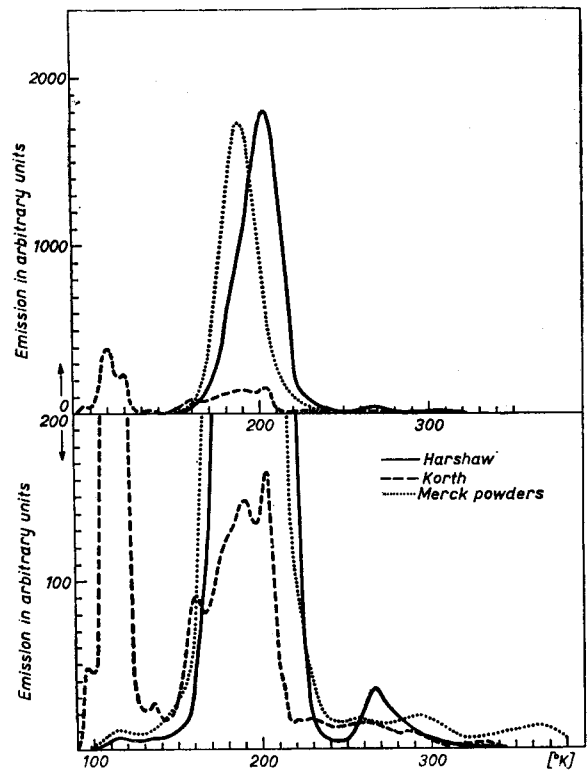


Fig. 9. Thermoluminescence emission between 200-800 mμ in different NaF samples

Moreover, there is no reproducibility for samples of different origin. One must thus conclude that thermoluminescence measurements fail to yield trustworthy information on the location and number of traps characteristic of NaF pure crystals. Those engaged in thermoluminescence measurements are well aware of this difficulty. The case of NaF, however, is still worse, because here not only the traps, but also the recombination centres depend on the sample; the emission spectra for the same glow peaks which we investigated in the spectral range 200–800 m $\mu$  show remarkable differences while other alkali halides (*e.g.* KBr, see communication by Fieschi, Panizza and Scaramelli) show no disagreement.

#### 4. Discussion

The enormous amount of work devoted to the effect of ionizing radiation on the creation of colour centres has brought us to a rather clear understanding of the behaviour of alkali halides at LHeT, and to some plausible models at higher temperatures [12]. In the mathematical description of the growth curves for the coloration one has sometimes introduced bleaching terms acting during the  $X$ -ray irradiation, proportional to the momentary concentration of  $F$  centres (*e.g.*  $dn_F/dt = bn_{\text{vac}} - an_F$  [13], similar terms have been invoked also in order to explain the slow growth of the  $Z_1$  band [14], and the bleaching of the complex bands under  $X$ -irradiation [15]. Lütty [16] discussed the elementary processes that can contribute to the coloration; his results on the  $X$ -ray coloration of untreated and of additively coloured KBr show that, at temperatures where  $F'$  centres are unstable, preexisting  $F$  centres do not affect the rate of formation of new centres: the bleaching terms, if present, are very weak. On the other hand older measurements by Harten [17] and by Jaffe [18] show that both electric current and electric pulses induced by ionizing radiation are affected by the presence of  $F$  centres; this suggests once more that colour centres,  $F$  or  $F'$ , have an appreciable cross-section for the capture of electrons or of holes.

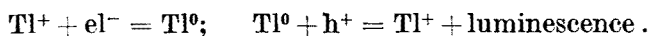
Since capture of free carriers by vacancies or by colour centres can in principle yield emission of a photon, the complicated processes associated with the generation of colour centres can be investigated also by following the changes in emission. Although many papers are available on the luminescence induced by  $X$ -ray irradiation, we do not know of any attempt to correlate absorption and emission measurements at increasing doses of irradiation.

As already stated, NaF was chosen because in it the colour centre luminescence bands appear in a spectral region more easily detectable than for chlorides or bromides. The drawbacks are that the properties of NaF are practically unknown, and that the samples available are not sufficiently pure.

In principle we may expect two kinds of capture processes, while the crystal is being irradiated:

A. Free carriers are captured by vacancies or other imperfections, to form new centres; this is the case for the  $F$  centres produced when newly formed vacancies trap conduction electrons.

B. A recombination process takes place at a preexisting colour centre, or at an impurity, by successive capture of an electron and a hole (or the reverse), leaving the situation unchanged: this occurs most probably *e.g.* in salts activated with thallium, according to a process of the following kind:



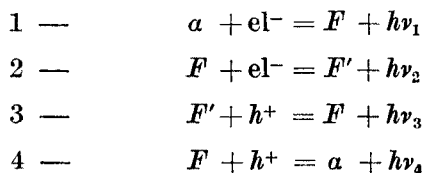
The frequency of these processes under  $X$ -irradiation is, of course, proportional to the number of free carriers, to that of trapping centres, and to the capture cross-sections. It is known *e.g.* that negative ion vacancies ( $\alpha$ -centres) and  $F$  centres have a large cross-section for capturing electrons. The possibility of having photon emission depends on the probability of radiative transition.

Radiative processes of the type A, if present, should yield an emission intensity  $L$  proportional to the rate of production of new centres, while for the case B emission should be proportional to the number  $n_c$  of centres present at any given instant in the crystal.

$$a = L \propto dn_c/dt,$$

$$b = L \propto n_c.$$

Let us consider the electronic colour centres; in principle we might have the following processes:



plus similar effects for the  $M$  centres. Process 1 should occur with emission of a quantum  $h\nu_1$  of the same energy as that of  $F$  photoemission. Process 4, if appreciable, justifies the bleaching term introduced by Smoluchowski; the free vacancy would successively recapture an electron, and we should have recombination of type B, with emission intensities proportional to the number of  $F$  centres present in the crystals; clearly we do not know whether process 4 is radiative, and know nothing of the energy of the photon  $h\nu_4$ .

Analogous mechanisms can be introduced for other centres.

The results obtained by us do not give definite indications on the actual emission process. What can be said is the following: the low temperature behaviour of the so-called  $F$  emission rules out the possibility of type B processes; after some minutes of  $X$ -irradiation the luminescence intensity, in fact,

becomes constant, suggesting a relation  $L_F \sim dn_F/dt$  because in the same range of temperatures the  $F$  centre concentration increases linearly. However, the intensity in Korth crystals is about the same as in Harshaw crystals, while the rate of production of new centres is greater in Korth NaF. A second difficulty resides in the interpretation of the changes in emission intensity during the initial stage of irradiation. The absence of RT emission at  $785\text{ m}\mu$  could be due to the fact that, as in other alkali halides, the decay process is non-radiative at high temperatures. Before definite conclusions can be drawn, however, further research is needed in order to assign with certainty the  $F$  centre photoluminescence.

The behaviour of the  $M$  emission is still more puzzling: at RT the luminescence intensity grows monotonically, starting from zero, hence suggesting a number of emitters proportional to the number of colour centres (a mechanism of type B); the growth curves for absorption and emission, however, do not fit; moreover, when after  $X$ -irradiation at RT the temperature is lowered, the emission decreases to zero, while the number of  $M$  centres initially increases slightly, as one can see from the absorption measurements.

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