

## IMPURITY EFFECTS AND RADIATION DAMAGE. \_\_\_\_\_

### Kinetics of $U_2$ to $H_2O^-$ defects conversion in $OH^-$ doped KCl and KBr (\*)

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**Résumé.** — Un traitement thermique pulsé après la photodécomposition ultraviolette de défauts  $OH^-$  dans KCl et KBr a montré que le centre  $U_2$  prend une configuration intermédiaire avant que le défaut  $H_2O^-$  soit formé. Cette configuration est caractérisée par une bande d'absorption optique à  $45\,000\text{ cm}^{-1}$  pour le KCl et à  $40\,000\text{ cm}^{-1}$  pour le KBr. Après des observations expérimentales, on propose que la configuration soit formée d'une paire  $U_2 \cdot OH^-$  où le centre  $U_2$  a une absorption optique caractéristique et indépendante. Un cycle complet de procédés de génération et d'annihilation de défauts d'hydrogène dus à la photodécomposition du  $OH^-$  a montré que environ 95 % de la concentration initiale de  $OH^-$  a été restituée.

**Abstract.** — A stepwise annealing procedure after a UV photodecomposition of  $OH^-$  defects in KCl and KBr showed that a  $U_2$  center assumes an intermediate configuration before finally forming a  $H_2O^-$  defect. This configuration is characterized by an optical absorption band at  $45\,000\text{ cm}^{-1}$  in KCl and at  $40\,000\text{ cm}^{-1}$  in KBr. From experimental observations it is proposed that this configuration is formed by a  $U_2 \cdot OH^-$  pair with the  $U_2$  center having an independent characteristic optical absorption. A complete cycle of creation/annihilation process of hydrogen defects originated from the  $OH^-$  photodecomposition showed that nearly 95 % of the initial concentration of  $OH^-$  could be restored.

Substitutional  $OH^-$  ions in alkali halides undergo a photoionization process at low temperatures that directly produces interstitial hydrogen atoms ( $U_2$  centers). Since hydrogen defects are the simplest extrinsic imperfections a crystal can host,  $OH^-$  doped alkali halides are ideal systems for the study of point defects directly and indirectly produced by this solid state photochemistry. One of the very interesting defects that can be created at the expenses of the  $OH^-$  photodecomposition is the  $H_2O^-$  center or *wet F center* as was initially called [1]. In KCl it can be directly produced at 150 K by UV irradiation into the  $OH^-$  band at a temperature where  $U_2$  centers are thermally unstable, or *via* a stepwise procedure of producing stable  $U_2$  centers followed by a thermal assisted process of association between an  $OH^-$  impurity and an  $U_2$  center. In this work we report the results of a phenomenological investigation on the thermal stability of the intermediate defects that are created at the expenses of the initial products of the  $OH^-$  photodecomposition. The full kinetics of production and destruction of  $H_2O^-$  defects has been analysed for KCl and KBr crystals doped with  $OH^-$ .

The experimental methodology followed a standard low temperature procedure utilizing an optical cryostat for absorption measurements. Low temperature at the sample was obtained with a Janis 8DT

cryostat provided with windows allowing perpendicular optical paths and a gas exchange chamber as a thermal switch. Optical absorption measurements were made with a Zeiss DMR 21 and a PE 180 spectrophotometers. High quality crystals were provided by the Utah Crystal Growth Laboratory. Temperature was controlled and measured with copper constantan thermocouples using an ice point as the zero degree reference.

After an initial 35 % dissociation of  $OH^-$  into  $U_2$  and  $O^-$  centers the samples were pulse annealed over a wide range of temperatures but in small intervals so that intermediate products could carefully be detected and identified previously to the  $H_2O^-$  formation. In KBr the initial optical dissociation of the  $OH^-$  defect and the subsequent heat treatments produced the spectra showed in figure 1. A similar spectra was obtained for KCl and in both crystals three main regions of thermal stability were clearly characterized after a series of heat pulses that finally restored 95 % of the original  $OH^-$  concentration. All bands that could be resolved after the heat treatments have their maxima plotted against the temperature of treatment in figure 2 for KBr.

The first main change in the thermal stability of the defects produced by the  $OH^-$  photodecomposition is the  $U_2$  center thermal destruction. In KBr the 100 K heat pulse produced a new absorption band at 4.97 eV (250 nm) with 0.26 eV FWHM located at the high energy side of the  $U_2$  band and denominated

(\*) Work supported by FAPESP and CNEN.

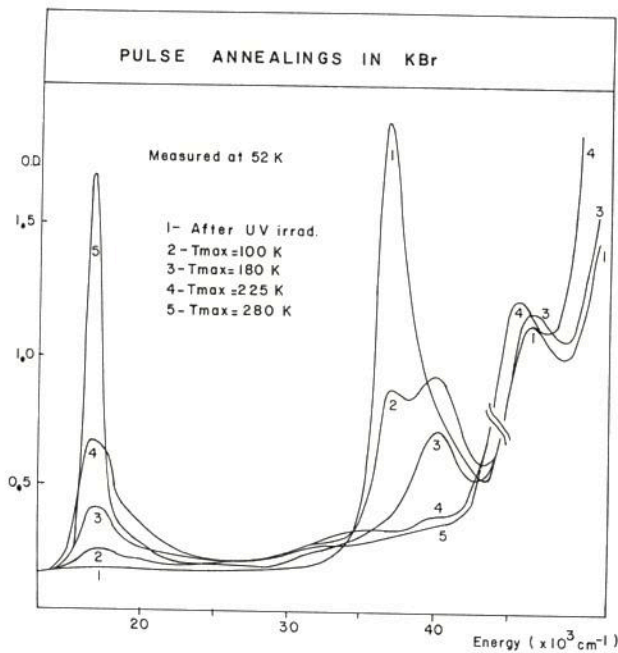


Fig. 1. — Spectra of KBr : OH<sup>-</sup> after several pulse annealings at different temperatures. The formation of the U<sub>2x</sub> band is shown after an anneal at 100 K.

as U<sub>2x</sub>. This band appeared simultaneously to the absorption of the H<sub>2</sub>O<sup>-</sup> center that is already produced at this stage. Apparently these two bands are formed in a competing way at the expenses of the U<sub>2</sub> center since the maximum rate of destruction of this center coincides with the maximum rate of formation of the other two. Although almost coincident with the U<sub>2</sub>' band — a spin orbit component of the U<sub>2</sub> — the U<sub>2x</sub> band behaves differently from it. The U<sub>2x</sub> band does not get reduced as the U<sub>2</sub>' does when the U<sub>2</sub> center is thermally destroyed.

After this main transformation of U<sub>2</sub> into U<sub>2x</sub> and H<sub>2</sub>O<sup>-</sup> it was observed a region of relative thermal stability for these two bands, the U<sub>2x</sub> being relatively longer lived in the KBr sample. A thermally activated OH<sup>-</sup> emission process due to the recombination of U<sub>2</sub> with O<sup>-</sup> centers was also observed [2]. A second drastic change of the thermal stability of the centers involved in this study occurs at 130 K for KCl and at 180 K for KBr. Further heat pulses to these temperatures showed that now U<sub>2x</sub> bands are thermally erased at the same time that more H<sub>2</sub>O<sup>-</sup> centers are created. In KBr this second step where H<sub>2</sub>O<sup>-</sup> is formed, competes with U center formation while for KCl only the H<sub>2</sub>O<sup>-</sup> band is formed.

H<sub>2</sub>O<sup>-</sup> centers are finally destroyed thermally at 220 K for KCl and at 250 K for KBr. In KCl it is observed the formation of U, OH<sup>-</sup> and F bands at the expenses of the H<sub>2</sub>O<sup>-</sup> band while in KBr only the F band is finally produced. As a last procedure to verify the reversibility of the described phenomena the samples were left at room temperature in the dark for several days to verify if all final products would transform back into OH<sup>-</sup> defects. F and U bands

were destroyed after this period and an overall return of 95 % of the original OH<sup>-</sup> concentration was observed for both samples.

After these general phenomenological observations, the kinetics of creation and destruction of the defects described above was analysed. As it is immediately characterized in figure 2 the observed kinetics was

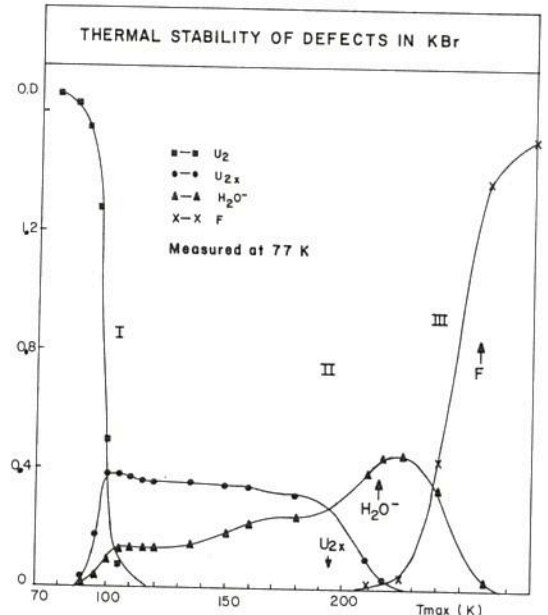


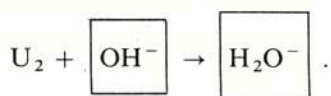
Fig. 2. — Behaviour of the band maximum at 77 K after several annealings at different temperatures.

divided into three temperature stages, that occur when U<sub>2</sub>, U<sub>2x</sub> and H<sub>2</sub>O<sup>-</sup> centers are respectively destroyed. To obtain the relative concentration of the defects participating in each stage the total oscillator strength of the H<sub>2</sub>O<sup>-</sup> was estimated. Assuming for KBr that the thermal destruction of H<sub>2</sub>O<sup>-</sup> brings only F centers and interstitial water molecules in a one to one ratio as no other absorptions were observed, we obtained the value of 0.62 for the total *f* number of the H<sub>2</sub>O<sup>-</sup> center. This value was further confirmed by an experiment where this center was photodissociated at 50 K in KCl and only U<sub>2</sub> and OH<sup>-</sup> centers were produced in a one to one ratio. For the second stage the same method was used to compute the *f* number of the U<sub>2x</sub> center since when thermally destroyed, it produced H<sub>2</sub>O<sup>-</sup> and U bands. Its *f* value was found to be of 0.35. These numbers were obtained utilizing the relation :

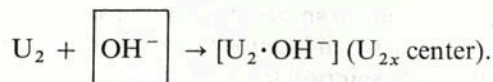
$$\frac{N_x f_x}{N_y f_y} = \left[ \frac{n}{(n^2 + 2)^2} \right]_x \left[ \frac{(n^2 + 2)^2}{n} \right]_y \frac{\left[ \int k d(h\nu) \right]_x}{\left[ \int k d(h\nu) \right]_y}$$

After obtaining these *f* values, the first two thermal stages were analysed only for KBr since the U<sub>2x</sub> band is not well resolved in KCl. In the first stage,

stable  $U_2$  centers when made unstable by thermal activation, recombine with available  $U_2$ ,  $O^-$  or  $OH^-$  centers leading to competing recombination mechanisms. This competing character is mainly due to distinct spatial correlations between pairs of centers involved in the recombination. The recombination with the  $O^-$  centers, however, is only indirectly observed since the decrease of the  $O^-$  band occurs in parallel with the  $OH^-$  characteristic luminescence. This thermally stimulated emission is not followed by an increase in the  $OH^-$  band as it would be expected since  $OH^-$  defects are being restored at this stage. The formation of the  $H_2O^-$  center accounts for 15% of the  $U_2$  centers destroyed and this recombination channel follows the same direct kinetics proposed earlier by Rush and Seidel [1] for KCl as :



The formation of the  $U_{2x}$  center, the other product of this first stage, brings a new configuration that is stabilized prior to the formation of the  $H_2O^-$  in the second stage. In this way a  $U_{2x}$  center is here proposed as a  $U_2$  center stabilized at a higher temperature, close to an  $OH^-$  impurity, similarly to the stabilization of an H center close to an aliovalent impurity forming an  $H_A$  center. The  $U_2$  center is not directly trapped by the  $OH^-$  impurity but forms with it a molecular defect such as  $U_2 \cdot OH^-$  with independent electronic absorptions for the individual components. This recombination channel is here represented by the reaction :



From a concentration balance of all products involved in this first stage  $U_{2x}$  centers account for 35% of the  $U_2$  centers thermally destroyed. The remaining 50% of the  $U_2$  centers that disappear leading to no observable optical absorption may have recombined among themselves in a pairwise way to produce undetectable  $H_2$  molecules.

In the second thermal stage, an almost equal number of  $H_2O^-$  and U centers are formed at the expenses of the  $U_{2x}$  destruction. Utilizing the same

assumptions and the  $U_{2x}$  model proposed for the first stage and taking the relative absorption strengths of all the centers involved, it is obtained that the destruction of  $U_{2x}$  centers leads approximately to 45% of U centers and 55% of  $H_2O^-$  centers. The hydrogen atom thermally freed is either trapped by the  $OH^-$  impurity or by displacing the OH molecule gets trapped by its vacancy, traps its electron and forms a U center.

In the third thermal stage the destruction of the  $H_2O^-$  center leads, in KBr to F center formation only, while in KCl, U and  $OH^-$  centers are preferentially formed over F centers in a 4 : 2 : 1 ratio. This concentration ratio is obtained by weighing the areas under the absorption curves and considering the previously estimated  $f$  numbers.

After a prolonged anneal at 300 K both samples showed a 90 to 95% reconstitution of the original concentration of  $OH^-$  impurities. Taking into account that the  $O^-$  defect is always present in the sample after the initial  $OH^-$  break up, many undetectable reactions may take place at these high temperatures. Thus, centers such as F and U, indirectly produced from the original  $OH^-$  photodecomposition, cannot be stabilized at room temperature for example, due to the presence of other thermally unstable products as OH or  $H_2$  molecules or  $O^-$  ions.

From the observed reaction kinetics some conclusions and propositions can be made : a) the  $U_{2x}$  center is an intermediate configuration of the  $U_2$  center close to an  $OH^-$  impurity, before it gets definitely trapped forming the  $H_2O^-$  defect, b) the 95% recovery of the original  $OH^-$  concentration after the thermal destruction of the  $H_2O^-$  centers does not favor the formation of stable  $H_2O$  molecules in interstitial sites as proposed by Rush and Seidel [1, 3] and c) the formation/destruction kinetics of the  $H_2O^-$  center indicates different binding energies for the two hydrogen atoms involved in this center for the temperatures considered in this work ( $T=77$  K). A final decision on whether the proposed model will hold is not possible with the present experimental data alone. ESR studies with temperature particularly looking into the main kinetic stages and a through IR investigation to detect possible vibronic modes will help to correlate effects and establish the validity of the proposed model.

## DISCUSSION

*Question.* — J. M. SPAETH.

From ESR measurements we have seen that the  $U_{2x}X$  centre is paramagnetic. MCD measurements also show that  $U_{2x}X$  is paramagnetic ?

*Reply.* — S. P. MORATO.

I am very glad to hear your comment. I would expect that the  $O_2X$  should show paramagnetism as

the  $U_2$  does. The interaction with the  $OH^-$  should bring information through the ESR signal that will allow us to settle for a precise configuration of the  $U_{2x}X$  center. I would suggest that KBr :  $OH^-$  is the best candidate for these studies.

*Question.* — G. BALDACCHINI.

A few years ago I tried with Prof. F. Luty to look

at the luminescence of the wet F centre,  $\text{H}_2\text{O}^-$ , unfortunately the centre is not stable at any temperature under irradiation (laser). Do you know any method to stabilise this kind of centre?

*Reply.* — S. P. MORATO.

Yes, in fact we are doing the photodecomposition of the  $\text{H}_2\text{O}^-$  defect right now. These studies are showing that with very low light levels the decomposition is highly efficient and almost temperature independent process. To have any chance of observing its luminescence you will have to operate with low intensity excitation, similar to the  $\text{OH}^-$  case.

*Question.* — M. IKEYA.

We have recently observed the ESR spectrum of the interstitial hydrogen atom perturbed by  $\text{OH}^-$

in KF. No such spectrum is observed in KCl and KBr presumably because of the large lattice separation. The  $\text{H}_i^0$  is surrounded by  $4\text{F}^-$  and  $\text{OH}^-$  is at the next shell. Therefore, your assignment might be correct. Did you observe the enhancement of the back-ground optical absorption? If you have observed it, this might be associated with the hydrogen voids. Our calculation using Mie theory shows that voids give broad absorption in alkali halides and hydrides due to the light scattering.

*Reply.* — S. MORATO.

We in fact did observe an enhancement of the UV absorption background with a slight structure showing up in the general hole center region. This absorption could also be due to the  $\text{OH}^0$  molecules that are left out of some portion of our general kinetic process.

#### References

- [1] RUSH, W. and SEIDEL, H., *Solid State Commun.* **9** (1971) 231.
- [2] KOSTLIN, H., *Solid State Commun.* **4** (1965) 81.
- [3] RUSH, W. and SEIDEL, H., *Phys. Status Solidi* (b) **63** (1974) 183.