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 cm^{-1} pour le KCl et à 40 000 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 cm^{-1} in KCl and at 40 000 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/anihilation 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 kinectics 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 a absorption band at 4.97 eV (250 nm) with 0.26 fo FWHM located at the high energy side of the U_2 band and denominated

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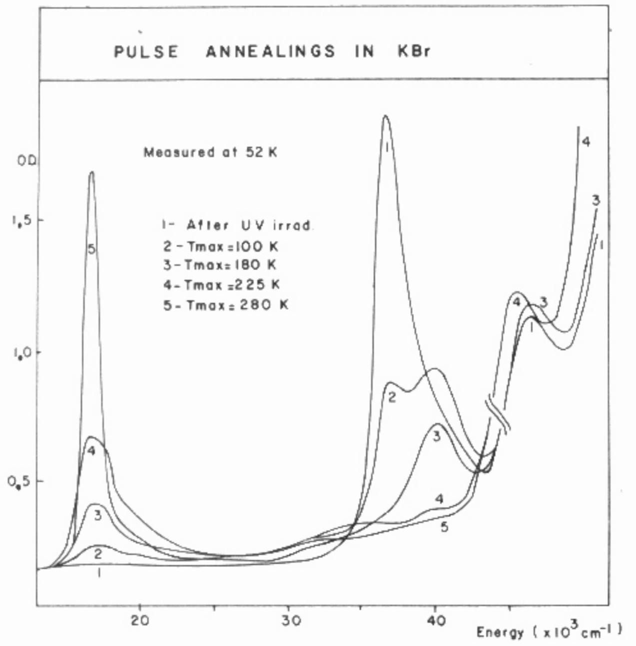

Fig. 1. — Spectra of KBr : OH^- after several pulse annealings at different temperatures. The formation of the U_{2x} band is shown after an anneal at 100 K.

as U_{2x}. This band appeared simultaneously to the absorption of the H_2O^- center that is already produced at this stage. Apparently these two bands are formed in a competing way at the expenses of the U_2 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_2'' band — a spin orbit component of the U_2 — the U_{2x} band behaves differently from it. The U_{2x} band does not get reduced as the U_2'' does when the U_2 center is thermally destroyed.

After this main transformation of U_2 into U_{2x} and H_2O^- it was observed a region of relative thermal stability for these two bands, the U_{2x} being relatively longer lived in the KBr sample. A thermally activated OH^- emission process due to the recombination of U_2 with O^- 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_{2x} bands are thermally erased at the same time that more H_2O^- centers are created. In KBr this second step where H_2O^- is formed, competes with U center formation while for KCl only the H_2O^- band is formed.

H_2O^- centers are finally destroyed thermically at 220 K for KCl and at 250 K for KBr. In KCl it is observed the formation of U, OH^- and F bands at the expenses of the H_2O^- 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^- defects. F and U bands were destroyed after this period and an overall return of 95 % of the original OH^- concentration was observed for both samples.

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

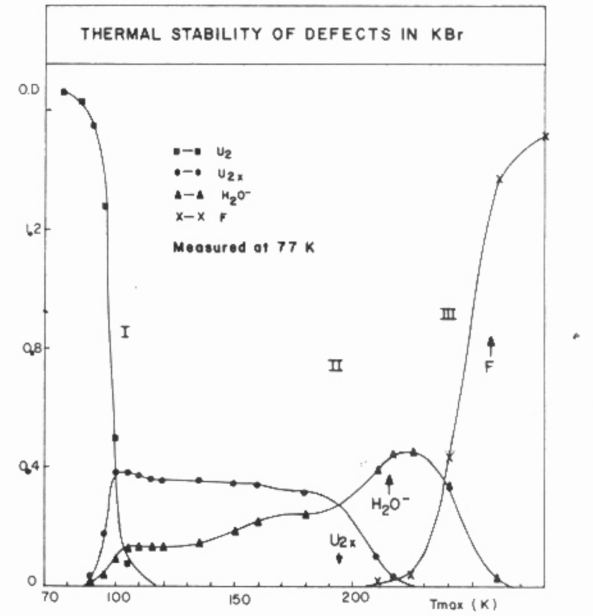

Fig. 2. — Behaviour of the band maximum at 77 K after several annealings at different temperatures.

divided into three temperature stages, that occur when U_2, U_{2x} and H_2O^- centers are respectively destroyed. To obtain the relative concentration of the defects participating in each stage the total oscillator strenght of the H_2O^- was estimated. Assuming for KBr that the thermal destruction of H_2O^- 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_2O^- center. This value was further confirmed by an experiment where this center was photodissociated at 50 K in KCl and only U_2 and OH^- 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_{2x} center since when thermally destroyed, it produced H_2O^- 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_{2x} band is not well resolved in KCl. In the first stage, stable U_2 centers when made unstable by thermal activation, recombine with avaliable 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 kinectics proposed earlier by Rush and Seidel [1] for KCl as :

$$U_2 + \boxed{OH^-} \rightarrow \boxed{H_2O^-} .$$

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 :

$$U_2 + \boxed{OH^-} \rightarrow [U_2 \cdot OH^-] \; (U_{2x} \text{ center}).$$

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 disapear 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 strenghts 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 kinectics 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 kinectics 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 kinectic 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, H_2O^-, 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 H_2O^- 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 OH^- case.

Question. — M. IKEYA.

We have recently observed the ESR spectrum of the interstitial hydrogen atom perturbed by OH^- in KF. No such spectrum is observed in KCl and KBr presumably because of the large lattice separation. The H_i^0 is surrounded by $4F^-$ and 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 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.