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ABSTRACT

Atom hydrogen in neutral (H^O) and negative (H^-) form on substitutional and interstitial lattice sites gives rise to well characterized model defects in alkali halides $(U, U_1, U_2, U_3$ centers), which have been extensively investigated in the past. When studying the photo-decomposition of OH^- defects, a new configuration of atomic charged hydrogen was discovered, which can be produced in large quantities in the crystal and is apparently not connected to any other impurity. This new hydrogen defect does not show any pronounced electronic absorption, but displays a single sharp local mode band (at 1114 cm^{-1} in KCl) with a perfect $\sqrt{2}$ H→D isotope shift. The defect can be produced by various UV or X-ray techniques in crystals doped with OH^-, SH^- or H^- defects. A detailed study of its formation kinetics at low temperatures shows that it is primarily formed by the reaction of a mobile Cl_2^- crowdion (H-center) with hydrogen defects.

1 – INTRODUCTION

Hydrogen impurities alkali halide crystals are well studied entities in their configuration and properties. So far there are only four known basic forms of hydrogen centers in these lattices. Occupying one anion site we can either have an hydrogen ion (H^- or U center as more commonly known[1,2]) or a hydrogen atom (H^O or U_1 center[3]). In interstitial positions we can have again an hydrogen ion (H_i^- or U_1 center[4]) or an hydrogen atom (H_i^O or U_2 center[5]). All these forms of hydrogen centers are very accessible to a full study with optical and magnetic techniques that detect their electronic or vibrational transitions or even a possible paramagnetic character as shown by the U_2 center for example. Hydrogen interstitials created by "optical radiation damage" through photodissociation of substitutional OH^- or H^- impurities have played and still play a model rule in the attempt to understand both the primary process and secondary reactions of the formed interstitials. In the case of the H^- defect, an "extrinsic changed Frenkel pair" consisting of anion vacancy and H_i^- (instead of the Cl_i^-) is formed. The H_i^- defect gives rise to a very broad structureless electronic absorption in the UV and to a local mode absorption in the IR (around 12μ for KCl). This latter displays at lowest temperatures, a fine structure consisting of several groups of sharp lines that correspond to H_i^- with various special correlations and interactions to the anion vacancy, or "correlated extrinsic Frenkel pairs" (the H_i^- local modes are split by the interactions with the anion-vacancy). The thermal stability of the H_i^- center shows the same behaviour of the intrinsic chlorine interstitials: thermal annealing curves with characteristic steps are observed. A first sharp annealing step corresponds to the extinction of the specially correlated extrinsic Frenkel pairs. A higher temperature annealing step corresponds to the extinction of the free uncorrelated H_i^- defect.

Several "perturbed hydrogen centers" with the hydrogen located close to other impurities have been studied recently. Specially correlated U-H center pairs were found to display a broadening and shifting of the U center UV absorption and a removal of the degeneracy of its IR local mode absorption[6]. Pairs of mutually perturbed U centers ($H^- H^-$ pairs) were also the subject of recent

investigations[7]. These < 110 > oriented H⁻H⁻ pairs produce several lines in the IR local mode region that could be interpreted with coupled oscillator models. The presence of additive metallic impurities can also produce other forms of perturbed hydrogen as the U_A (Na⁰) center[8]. For example, a metallic impurity like Na⁰ in KCl situated in one of the six nearest neighbor sites of an H⁻ center (then a U_A center) will cause the splitting of the triply degenerate local mode vibration of the H⁻ center. This splitting is due to the reduction of the O_h symmetry of the perfect lattice into C_{4v} symmetry.

2 – EXPERIMENTAL PROCEDURES

The KCl single crystal preparation and the experimental optical techniques have already been described in detail in the preceding work[9]. To additively color our samples we employed the method described by Van Dorn[10] with some modifications. In this method the F center concentration was obtained by a controlled vapor pressure of the metal vapor using an excess pressure of nitrogen gas. We used a low fixed pressure of nitrogen gas and varied the liquid potassium temperature, thus varying its vapor pressure. Using an intermediate calibration curve from Van Dorn and Rogener's methods[11], which gives the F center concentration as a function of the potassium vapor pressure, we were able to obtain quite reproducible F center concentrations on the order of 10^{16} to 10^{18} cm⁻³. Hydrogenation of an additively colored sample consists in the controlled diffusion of hydrogen into the crystal under high temperature and hydrogen pressure. By heating the crystal at 650°C under 20 atmospheres of hydrogen gas, hydrogen molecules diffuse into the crystal and react with the F centers, producing substitutional hydrogen ions (U centers).

To irradiate our samples with X-Rays at low temperatures the cryostat head was provided with a fifth window made of a 1 mm thick aluminium foil at 45° bisecting the perpendicular optical paths. The X-Ray source was a Horelco with a W target. The unfiltered exit window placed at approximately 5 cm of the sample. The X-Ray exposure was always at 30 KV and 20 mA.

To investigate all the transparent range of the crystal with UV, V is and IR spectroscopy — especially in the hydrogen center local mode region we set up two experiments with the two parallel and perpendicular geometries using crystals of suitable dimensions. The aim was to produce the same photochemical reactions in both samples in parallel so we could carefully detect and correlate any IR effects to the already known spectral behavior in the UV region.

3 – RESULTS AND DISCUSSIONS

As it was shown in the previous work[9], a sequence of UV irradiations at LNT in KCl:OH⁻ system suggested that a missing Cl_i^0 crowdion was being trapped at some unknown form of hydrogen defect undetectable by UV or visible spectroscopy. With the changes in geometry previously described we set up an experiment that would show all the effects of this UV irradiation sequence at LNT by monitoring all the changes in the optical absorption of the KCl band gap.

3.1 – Photoproductions of a New Hydrogen Center

As shown in figure 1A we started with the photodissociation of the OH⁻ defect by irradiating monochromatic UV light at 204 nm (OH⁻ absorption band). As a result we observed in the UV range the OH⁻ → H_i^0 conversion as previously described. In the IR range no significant spectral changes can be observed at this stage, as expected. The OH⁻ stretching vibration absorption at 2.7μ is too weak to be detectable for the low OH⁻ doping used, and the neutral H_i^0 interstitial does not give rise to an optical active local mode. In the next step we photo-destroyed H_i^0 centers, reproducing our former UV spectral results. In this irradiation stage, new pronounced effects developed in the IR range. Besides the appearance of the H⁻ local mode transitions — as expected from the UV result — we observed the growth of a new single band so far not reported in the literature. This band has its maximum at

1112 cm^{-1} (at LNT), at a 30% higher energy compared to the H_i^- center local mode transition. We call the center responsible for this new hydrogen local mode absorption tentatively H_x^-, with the "x" indicating its unknown structure and site, and the minus sign indicating that this new center should be charged by being IR active.

Proceeding with the series of spectral irradiations showed in Figure 1, we illuminated in the third stage with U-band light, producing the well known $H^- \to H_i^-$ conversion. This step basically did not change the optical density of this new center. As expected we observed in both ranges (IR and UV) the decrease of the H^- center (U band) and besides the increase of the H_i^- center, the U band destruction is also responsible for some H_i^0/F center pairs formation. The new H_x^- defect apparently does not participe in all these transformations. A further U_2 band irradiation was performed in case B, mostly to follow in the IR the behavior of the new H_x^- band. The major effects after this irradiation were the increase of the H^- center, the increase of the H_x^- band and a decrease of the H_i^- centers. A decrease of the H_i^- center could partially be explained by the fact that U_2 band irradiation also reaches the U_1 electronic absorption band which is very broad and extends from 280 to 230 nm in the far UV. We should point out here that in a similar set of experiments with a KCl:OH$^-$ + Na$^+$ crystal, the monochromatic U_2 band irradiation only brought up H_A centers as mentioned before with no traces of H_x^- center formation whatsoever in the IR region.

All the above described effects can happen simultaneously if we irradiate the crystal with undispersed UV light. This was indeed observed by irradiating two KCl samples of different OH$^-$ concentrations. For the low OH$^-$ concentration sample we observed a parallel rise of the H_x^-, H_i^- and H^- center transitions (Figure 2A). After a prolonged irradiation these transition bands reached some sort of dynamical equilibrium and saturated. In several attempts we disturbed this dynamical equilibrium by illumination with monochromatic light into the U band for example, producing the $H^- \to H_i^0 + \square$ conversion already described in Figure 2B. Conversely we would invert this process by illuminating into the U_1 band. While the relative amounts of H^- and H_i^- local mode absorptions changed reversibly in these tests, the height of the H_x^- transition band remained approximately constant (as it did in the experiment) shown in Figure 1B. At the end we were able to return to the dynamical equilibrium relative heights of these three transitions as shown in Figure 1A just by repeating for a few hours the full Xenon lamp irradiation. The IR local mode transitions and the corresponding UV spectral absorptions after ten hours of undispersed light irradiations are shown respectively in Figures 2A and 3B. From the UV spectrum we can confirm that to new bands were found in the UV region. This is consistent with the fact that the H_x^-, apparently having no significant electronic transition in the transparent crystal range, will be the most prominent product of the OH$^-$ photodecomposition at LNT, as observed from this saturation experiment.

We repeated this full Xenon lamp irradiation experiment for a KCl:OH$^-$ + Na$^+$ sample (see Figure 2B) and observed the same saturation behavior as the one obtained with a KCl:OH$^-$ sample (Figure 2A). Since our irradiation also contains the wavelength which is absorbed by the H_A centers, this kind of undispersed irradiation prevents their formation. (We confirmed the photodestruction of H_A centers in another experiment where we bleached the H_A band by irradiating monochromatic light that is absorbed by the H_A center). As a result of this saturation experiment we again ended up with H_x^- centers as the most prominent band. For a higher concentrated KCl:OH$^-$ sample, under the same irradiation conditions, we were able to see in some more detail the initial build-up of these three transition bands (Figure 4). The initial formation rate of the H_x^- centers is low, but increases markedly under prolonged irradiation. This means that under undispersed irradiation conditions the H_x^- transition band is formed at the expense of another reaction product which must be initially created by the UV light irradiation component.

3.2 – H_x^- Local Mode Spectra and Isotope Effect H_x^- Formation in KBr:OH$^-$ and RbBr:OH$^-$ Crystals

A closer look at the H_x^- transitions band revealed very interesting features. It did not show any structure or splitting when cooled to low temperatures, displaying a single band with maximum at

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1114 cm^{-1} and a halfwidth of 2.5 cm^{-1} at 6K. The variation of the band shape as a function of temperature can be seen in Figure 5. Our general observations of the H_x^- center so far strongly indicate the presence of a hydrogen. But how would one confirm the presence of a hydrogen in this new defect? A rather straightforward test was to repeat the full Xenon lamp irradiation for a system such as KCl:OD⁻ and search for isotope shifts in the observed transitions. This experiment is described in Figure 6. We indeed observed the displacement of the H_x^- transition from 1112 to 779 cm^{-1}, an almost perfect $\sqrt{2}$ isotope shift (H → D). Parallel to this we also observed the isotope shift for the local mode of the H_i^- center from 845 cm^{-1} to 606 cm^{-1}. Finally, in a brief attempt to demonstrate the generality of the H_x^- defect and its photoproduction from OH⁻ defects, we took KBr:OH⁻ and RbBr:OH⁻ samples and repeated the full Xenon lamp irradiation experiment. We indeed found in these two systems the formation of H_x^- and H_i^- centers as in the KCl:OH⁻ system. For KBr:OH⁻ the peak positions of H_x^- and H_i^- were at 1095 cm^{-1} and 790 cm^{-1} respectively. For RbBr:OH⁻ they were at 1021 cm^{-1} and 745 cm^{-1} respectively. These results indicate the general nature of the H_x^- center excluding the possibility of its being formed only in KCl:OH⁻ systems.

Up to this point we know or anticipate that hydrogen and mobile Cl_i^o crowdions are the basic candidates for the formation of the H_x^- band. However we must remember that so far we only dealt with one of the two products of the OH⁻ photodissociation, namely the H_i^o center. In other words, the O⁻ center was never taken into consideration although it was always present and in the same quantities as the initial H_i^o center. In the full irradiation experiments, the presence of the O⁻ center is even more critical since here we are also irradiating in the O⁻ band. This could result in photochemical reaction of new defect aggregations. Since the precise optical detection of the O⁻ center and this contribution of the various defect reactions was experimentally impractical, its exclusion from the formation of the H_x^- center can only be proven by indirect experiments.

3.3 – The Formation of H_x^- Centers in KCl:H⁻

To answer all the pending questions that remained open up to this point we X-irradiated a KCl:H⁻ system at 77. The reasons to this are: a) X-rays are well known to produce Cl_i^o crowdions in KCl at low temperatures[12]; b) a KCl:H⁻ system would offer hydrogen traps for the mobile crowdions; c) a KCl:H⁻ system would exclude the presence of the O⁻ centers. We X-irradiated a KCl sample containing 5.6×10^{-1} H⁻. Due to the high concentration of H⁻ defects, its local mode transition was monitored by the anti Stokes phonon side band, since the main local mode transition is completely off scale (by a factor of ~40 higher than the phonon side band at LNT[13]). After a prolonged X-irradiation we observe the formation of structures correspond to transitions of H_x^- centers that have different spatial correlations to their anti centers – the anion vacancies – as explained by Fritz[4]. The X-irradiation also produces H_x^- centers as we had anticipated (Figure 7A).

In Figure 8A we display the growth and decay curves of the centers involved in Figure 7A. We observe that X-irradiation produces the following effects: a) H⁻ centers undergo a gradual reduction, reflected by the decrease of its phonon sideband; b) H_i^- centers measured by the main peak from the spatially uncorrelated ones are formed with approximately constant rate; c) H_x^- centers are formed initially with a small rate which increases under further X-irradiation. From C we recognize that H_x^- centers are formed more efficiently with the help of some reaction product that is obtained during the initial X-irradiation exposure. This observation makes the H_i^- center the strongest candidate for a trapping site for the Cl_i^o crowdions.

In order to further verify the participation of H_i^- defects in the H_x^- production process, we set up another experiment in which pre-exposed a KCl:H⁻ sample to UV irradiation. As a result of this UV irradiation we obtained, very efficiently, the H⁻ → H_i^- conversion process without any trace of H_x^- center formation (see Figure 7B). Under X-irradiation of this previously UV exposed sample, we observed an initial decrease of H_i^- centers and an increase of H_x^- centers with an initial formation rate a factor of ~ 16 larger than the initial H_x^- formation rate obtained by a direct comparison of Figure 20A with Figure 20B. Under further X-ray exposure the system tends to reach some dynamical equilibrium. The

observed facts confirm again strongly the pronounced participation of the H_i^- center as a trapping site for the Cl_i^0 crowdion. We cannot decide from these experiments if H_i^- defects play any role as the Cl_i^0 crowdion traps. We can however, conclude that if they participe in the formation process, this trapping probability for Cl_i^0 crowdion is considerably lower then that of H_i^- defects.

A doubt that emerges after doing these X-ray experiments may be expressed by the following question: Could the KCl:H⁻ sample contain unwanted OH⁻ impurities which would have produced the H_x^- effects under X-irradiation? Due to the high concentration of the H⁻ center, their UV absorption would completely mask any small OH⁻ band. Two conclusive arguments can be given against such a possibility:

a) The same UV light exposure which formed no H_x^- centers in the experiment of Figure 7B produced, in experiment shown in Figure 1. A an optical density of 0.15 in the H_x^- local mode absorption. If our KCl:H⁻ sample of experiment Figure 7B would have a factor of six lower concentration of OH⁻ impurity than experiment Figure 1A, we should have been able to produce 0.02 O.D. of H_x^- local mode absorption (0.02 O.D. was the lower limit of our detection system ability at the signal-to-noise ratio used). We can therefore say that if OH⁻ was present in the KCl:H⁻ sample it should be in concentrations less than 4×10^{-6};

b) In another experiment we exposed a sample of low OH⁻ concentration (2.5×10^{-5}) to X-rays at LNT during 16 hours and were unable to find any trace of H_x^-, H_i^- or H⁻ centers. This shows that X irradiation at LNT does not decompose at all the OH⁻ defect into any of the hydrogen reaction products H⁻, H_i^- and H_x^- as observed under UV irradiation of OH⁻. The participation of any unwanted OH⁻ additions in the experiments of Figures 19 and 20 is therefore definitely excluded, and so is the possible participation of any oxygen defects in the H_x^- formation.

For a further confirmation of the non-participation of the O⁻ center in the H_x^- formation we did another experiment in which we used a KCl:SH⁻ crystal and repeated the full UV irradiation treatment as we did with the KCl:OH⁻ crystal. We know from previous work[14,15] that the SH⁻ center can be also decomposed into S⁻ and H_i^0 defects. Proceeding with this full irradiation treatment we observed exactly the same H_x^- band in the KCl:SH⁻ crystal. The experiments described in this section, besides confirming, the participation of H_i^- and Cl_i^0 centers into the H_x^- center formation, ruled out completely and possibility of the participation of the O⁻ center in the H_x^- center production.

3.4 – Preliminary Conclusions About H_x^- Formation from LNT Experiments

Up to this point the various experiments at LNT allow us to draw several conclusions about the nature and formation process of the new H_x^- center: a) under full UV light irradiation, H_x^- centers are the most prominent hydrogen reaction products of the OH⁻ photodecomposition; b) under stepwise monochromatic OH⁻ photodecomposition, H_x^- defects from in the secondary stage by photoexcitation of H_i^0 centers. As this process creates mobile Cl_i^0 crowdions, the latter are very likely candidates for the H_x^- formation; c) The IR absorption of the H_x^- centers shows, by the H → D isotope shift, that it is caused by a perfectly localized vibration of a charged hydrogen ion; its single band structure indicates a site of high symmetry for the hydrogen, which does not split its local mode; d) H_x^- centers can be formed by X-irradiation of KCl:H⁻ crystals at LNT. This excludes any contribution of the oxygen in the H_x^- formation process, and confirms the idea that H_x^- centers are formed by the reaction of mobile Cl_i^0 crowdions with hydrogen defects. The increase of the initial H_x^- formation rate in this experiment by a previous H⁻→ H_i^- conversion makes the interstitial H_i^- defect the most likely candidate for the trapping of the Cl_i^0 crowdion forming the H_x^- center.

All the preceding experiments were done at LNT, where Cl_i^0 crowdions are mobile right after their creation and thus form the H_x^- defects instantaneously. If this picture is correct, we should be able to produce H_x^- centers in controlled steps at lower temperatures where Cl_i^0 crowdions are thermally stable. Experiments in this temperature range should therefore provide a

conclusive test on the formation process and a definitive identification of the hydrogen defect trapping the Cl_i^0 crowdion.

3.6 — Controlled Production of H_x^- Center at LHeT

We initially made the photodissociation of the OH^- center at 77K (for experimental convenience) by monochromatic 204 nm light (Step 0 in Figure 9A). We then proceeded with the further photochemical reactions at 6 K. After photodecomposing H_i^C centers (Step 1, Figure 9A) at 6K we observed that the H^- center local mode was built up as expected from previous experiments. In contrast to the corresponding experiment at LNT (see Figure 1), we observe at this step no trace of H_x^- (and H_i) formation. This confirms our previous assumption that the photodestroyed H_i^0 centers are quantitatively converted into H^- centers and Cl_i^0 crowdions, with the latter stabilized as H centers in the lattice. It further confirms our assumption that only mobile Cl_i^0 crowdions, reacting with hydrogen defects, are able to form the H_x^- centers. The "self-trapping" of the Cl_i^0 crowdions as H centers therefore prevents the H^- formation. If our line of arguing is right, the H_x^- centers should be formed if we make the produced Cl_i^0 crowdions mobile in some way. One way to achieve this is the optical excitation in the electronic transition (H band) of the Cl_i^0 crowdion, which leads to an optically stimulated motion of the defect. If we shine monochromatic light into the H band (Step 2 in Figure 9A), we indeed observe the appearance of the H_x^- local mode band. Simultaneously we see the reduction of the H^- local mode band. As no H_i^- defects have been present during this reaction we must conclude that in this step H_x^- defects have been formed by the reaction of "optically mobilized" Cl_i^0 crowdions with H^- defects. A further irradiation into the U_2 band (Step 3 in Figure 9B) proceeds with the $H_i^0 \cdot H + Cl_i^0$ formation as in Step 1 without further H_x^- formation. A subsequent monochromatic irradiation in the U band brought up mainly the local mode of the $H_i^-/[]$ close pairs (Step 4, Figure 9B) with the correspondent decrease of the H^- absorption center. Now that we have two kinds of hydrogen centers competing as trapping sites, we again optically bleach the H band and observe further increase of the H_x^- local mode band. Simultaneously we see a considerable reduction in the local mode absorption of the $H_i^-/[]$ close pairs, and a very small reduction in the H^- local mode. Apparently when both H^- and $H_i^-/[]$ pairs offered are much more effective for the H_x^- formation. This is exactly what we observed in the X-ray experiment with the $KCl:H^-$ crystals of LNT.

The second possibility to mobilize the Cl_i^0 crowdions after their optical creation at LHeT is a thermal annealing process into the temperature range of their thermal instability ($T > 55°$). This process was performed as Step 5 in Figure 9D. It leads to a further considerable increase of the H_x^- centers and a simultaneous destruction of the $H_i^-/[]$ close pairs. As the latter are clearly thermally stable in the used temperature range (they are thermally annealed only at $T > 90K^{[4]}$), we conclude that the H_x^- increase was achieved at the expense of the $H_i^-/[]$ close pairs. (The H^- centers remained approximately constant during the thermal annealing Step 5). Thus again we can conclude that thermally mobilized Cl_i^0 crowdions form H_x^- centers by reacting with $H_i^-/[]$ close pairs. The involvement of the Cl_i^0 in the H_x^- formation is conclusively demonstrated in Figure 10, in which we monitor the absorption during the thermal annealing process. The correspondence of the thermal destruction of the Cl_i^0 centers (around 55 K) to the increase of the H_x^- absorption is clearly demonstrated (the change in the H-band absorption at 10K is caused by thermal reorientation of the Cl_i^0 crowdions).

A more general experiment confirmed the two above described results. We employed undispersed broad band UV irradiation at 6K as we previously did at 77K. The results of this experiment are displayed in Figures 11A and 11B. From Figure 11A, Step 1, we see that after an exposure of undispersed UV light we observe immediate formation of all three hydrogen defects H_x^-, H_i^- (correlated and uncorrelated) and H^- centers. Since our irradiation contains the wavelenghts of the OH^- band, of the different hydrogen centers involved (H^-, H_i^-, H^0), and of the H band absorption of the Cl_i^0 center, the simultaneous appearances of the H_x^-, H_i^- and H^- centers is expected as in the LNT full irradiation case.

After this full UV exposure we bleached the H band using undispersed light but blocking any far UV light beyond 400 nm with a cut-off filter (see Step 2, Figure 11A). As previously observed, we

again see the raise of the H_x^- at the expense of H_i^- centers. The following step was to practically repeat previous UV treatment to re-establish the dynamical equilibrium among the three defects (Step 3, Figure 11A) as previously done at LNT. As a last step, we performed again the thermal annealing to 77K procedure to make the crowdions thermally unstable. After this treatment we again observed an increase of H_x^- centers, a decrease of H_i^- centers (both correlated and uncorrelated) and a corresponding decrease of H^- centers. This experiment, although being different in terms of irradiation procedures and intermediate products obtained, confirms the results of the previous monochromatic experiments.

3.6 -- The Thermal Destruction of the H_x^- Centers

To estimate the relative oscillator strength of the H_x^- center, we report to the previous work (Part I) where we learned that at LNT approximately 50% less H^- centers are formed when compared to the LHeT experiment. We assume that the other 50% of "missing" H^- centers are being consumed to form H_x^- centers. Using the relative strengths of the integrated absorptions in Figure 1B, we obtain $f_{H_x^-}/f_{H^-} \simeq 0.7$. Considering the value 0.5 for the oscillator strength of the H_x^- center. After we have studied the detailed kinetics of the H_x^- center creation and concluded that the H_x^- center was the final and optically stable products of the H_x^- thermal desctruction. When heating a sample containing H_x^- centers and following their local mode absorption at LNT after pulse annealing to various higher temperatures we found that the H_x^- centers decay thermally in the temperature range 180-210K (Figure 12). This annealing behavior is very close to the $H_i^- \rightarrow H^-$ thermal decay process of H_i^- interstitials described by Fritz[4]. We indeed observed, together with the extinction of the H_x^- centers, this thermal reaction $H_i^- + [] \rightarrow H^-$ by the H_i^- decrease and H^- increase, as shown in Figure 12A. A simple comparative analysis of the strengths of absorption changes in the three IR bands involved in this process shows that the extinction of H_x^- centers does not create H^- centers. Taking the loss in absorption strength in the H^- local mode (Δ OD 0.8) and converting it into the corresponding gain in absorption strength for the H^- center, we would expect an optical density increase of ~ 1.7 for the H^- absorption. We instead observed a mere 0.3 increase in O.D. of the H^- local mode, a fact that by itself excludes the possibility that the destruction of H_x^- centers will form H^- centers. The small increase of the H^- local mode is fully accounted for by the thermal destruction of the $H_i^-/[]$ extrinsic Frenkel pairs, as seen by the destruction of the H_i^- local mode band. No new local mode absorption in the IR range and no new electronic absorption in the UV/Vis range is observed to develop after the thermal destruction of the H_x^- defects.

3.7 -- Final Conclusions on the H_x^- Formation Process and Structural Model

The large variety of experiments described in the previous sections offered a consistent picture about the two components which participate in the dynamic H_x^- center formation process. We proved in different ways that Cl_i^0 crowdions are participating in the H_x^- center formation: a) in the LNT range, where U_1 band irradiation creates the H_x^- defects, we showed that competing Na^0 defects can capture and stabilize Cl_i^0 crowdions and suppress the H_x^- formation; b) creating Cl_i^0 crowdions by X-rays at LNT in a KCl:H$^-$ system leads to the formation of H_x^- (excluding the contribution of oxygen in any form in this process); c) at LHeT we were able to create H_x^- centers stepwise in a controlled way by first creating stable Cl_i^0 crowdions. Only when these crowdions were made mobile by optical or thermal excitation, the H_x^- defects appear.

The experiments under various temperature, irradiation, and defect conditions showed consistently the participation of hydrogen defects in the H_x^- formation process: a) in a crystal containing both $H_i^-/[]$ pairs and H^- defects, the formation of H_x^- centers is accompanied mostly by a reduction in close $H_i^-/[]$ pairs and very little, if any, by a H^- defect reduction; b) if only H^- defects are present, the H_x^- formation proceeds at the expense of the H^- defects. We therefore conclude that the H_x^- defect is formed by the reaction of mobile Cl_i^0 crowdions with either close $H_i^-/[]$ pairs (preferred process), or with H^- defects. As the $H_i^-/[]$ Frenkel pairs is - in terms of its net structural components - equivalent to the substitutional H^- defect, both these hydrogen traps for the Cl_i^0 crowdion can lead to the same end product. From the H_x^- local mode strength, spectral shape and isotope shift we concluded that the

defect must consist of a charged localized hydrogen defect in a site of high symmetry which does not split the local mode. The high frequency of the H_x^- local mode indicates a stronger vibrational potential of the H_x^- compared to the H_i^- defect. From the thermal destruction of the H_x^- center we know that it is not converted back into H_x^- centers, but disappears into some unknown optically inaccessible structure.

A structural model must be able to integrate and satisfy all these static and dynamic experimental features. We see only one possibility to achieve this in a single model: A hydrogen ion H^- in a body-centered interstitial position, with a trapped hole shared symmetrically by the four surrounding nearest neighbor anions (see Figure 13). This model first satisfies the observed static features, a localized charged hydrogen defect in a site of high symmetry with a single unsplit three-fold degenerate local mode transition. A side from the trapped hole, it is similar to the H_i^- defect (see Figure 13). In the latter one, the charged interstitial H_i^- defect will have strong electrostatic interactions with the surrounding ions, repelling and shifting outwards, the anions, and attracting and pulling inwards the cations. The addition of a hole (positive charge) to the shell of nearest neighbor anions in the H_x^- center will reduce the $H_i^- < > Cl^-$ repulsion and thus produce a closer distance between the hydrogen and the chlorine ions. As the potential for the localized vibration of the H^- is mainly produced by the Born-Mayer repulsion interaction with the (large size) anions, we will expect a higher local mode frequency of the H_x^- compared to the H_i^- defect. This is in agreement with the frequency shift to higher energies found experimentally.

For the dynamic formation process, we have to regard the two cases: a) reaction of a Cl_i^0 crowdion (an interstitial Cl_i^- ion with a bound hole) approaches a $H_i^-/\square$ Frenkel pair, the most natural process to assume is the recombination of the Cl_i^- interstitial with the empty vacancy of the Frenkel pair. As a result we are left with the H_i^- interstitial and the hole which was carried previously by the Cl_i^0 crowdion. If this hole just recombines with the interstitial H_i^- we would restore the original neutral interstitial H_i^0 center. Apparently, however, the polarization of the surrounding ions around the H_i^- defect (Figure 13) make it possible to trap the hole at the Cl^- ions surrounding the H_i^- defect in a stable way. b) reaction of a Cl_i^0 with a H^- defect in order to form the same H_x^- defect in this reaction, the approaching Cl^- interstitial crowdion will exchange the lattice place with the H^- defect, so that an interstitial H^- ion is formed. The hole, carried by the Cl_i^0 crowdion then gets bound to the H_i^- defect in the same way as above. In terms of its net components (after recombination of the hole with the H_i^- defect), the H_x^- is a neutral interstitial hydrogen atom. Thus when it gets thermally unstable and recombines with another H_x^- defect, it would form a neutral interstitial H_2 molecule. This defect is known to be present in alkali halides and spectrally invisible in both UV and IR range. The "spectral disappearance" of the H_x^- defect after thermal annealing is therefore understandable with our model.

We should point out that the proposed model is constructed strictly from an extended static and dynamic experimental material, which is conclusive and does not leave any alternative choice for a different model, consistent with the experiments. A theoretical justification for the proposed interstitial H^- structure with a stabilized hole shared by the surrounding anions is beyond the scope of this work. The theoretical understanding and justification for this peculiar "inverted and self-trapped exciton" at an interstitial hydrogen defect appears to be a challenging and interesting problem for further theoretical studies.

RESUMO

Átomos de hidrogênio negativos (H^-) ou neutros (H) quando em posições intersticiais ou substitucionais dão origem a defeitos mortos bem caracterizados nos haletos alcalinos (centros U, U_1, U_2, U_3) que tem sido extensivamente estudados no passado. Estudando-se a fotodecomposição de defeitos OH^- uma configuração nova de hidrogênio atômico carregado foi encontrada. Esta forma de hidrogênio pode ser produzida em grandes quantidades no cristal e não está aparentemente vinculada com nenhuma outra impureza. Este defeito de hidrogênio não apresenta nenhuma absorção eletrônica pronunciada mas apresenta um único modo local de máximo em 1114 cm^{-1} em KCl e com um desvio isotópico perfeito de $\sqrt{2}$ ($H + D$) Este defeito pode ser produzido por várias técnicas UV ou de raios X em cristais dopados com impurezas OH^-, SH^- ou H^-. Um estudo detalhado de sua cinética de formação à baixas temperaturas mostra que este defeito é primariamente formado da reação de um "crowdion" Cl_i^- (centro III) com defeitos de hidrogênio.
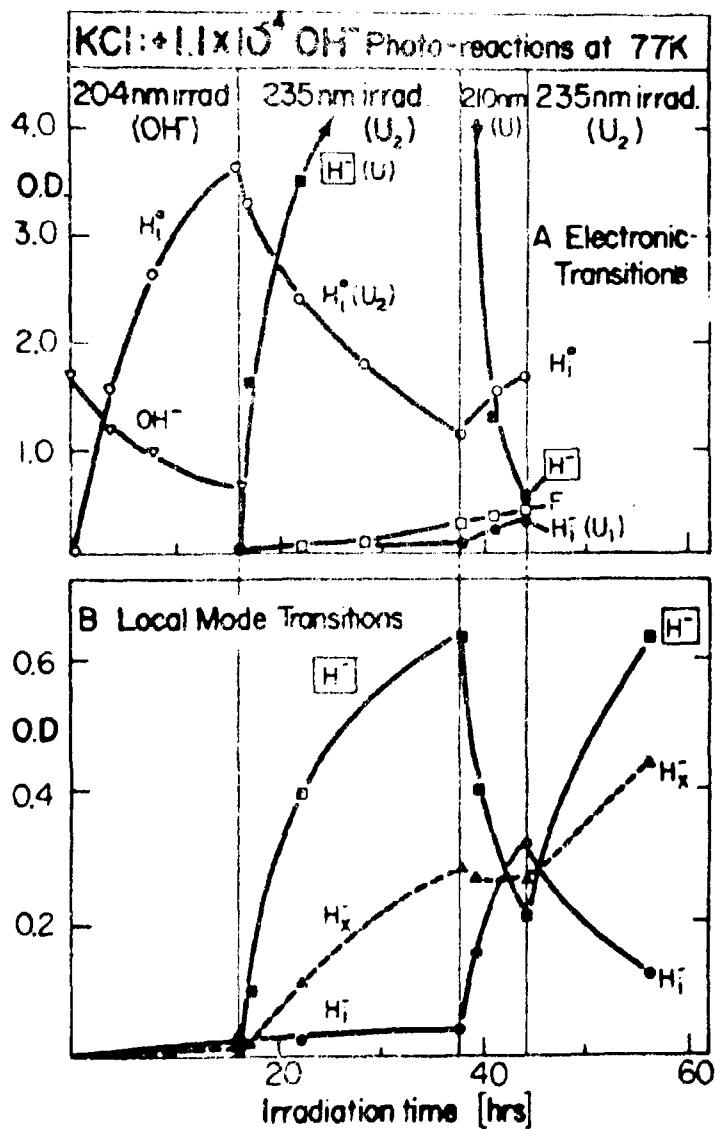
Figure 1 A — Electronic absorption bands as a function of irradiation time for a sequence of monochromatic irradiations in a KCl:OH crystal at LNT (thickness ~ 0.5 mm).

B — Local mode transitions in the IR for the same sequence of irradiations as in A (thickness ~ 8.0 mm).
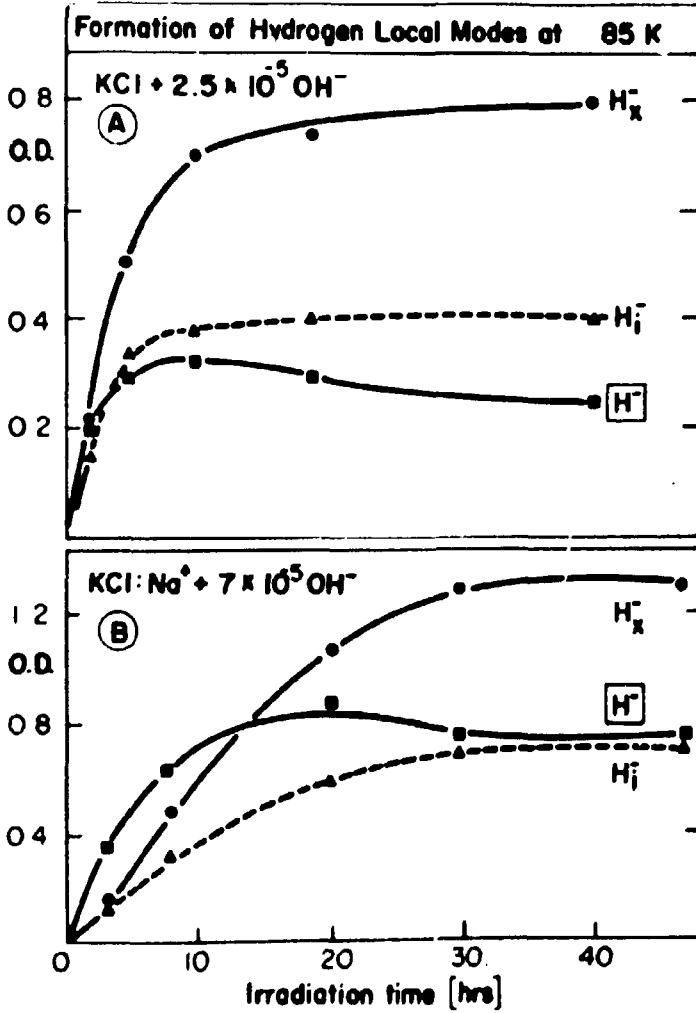
Figure 2 — Plot of the local mode transition of H^-, H_i^- and H_x^- centers as a function of irradiation time under full Xenon lamp irradiation at 85K (measured at 77K).

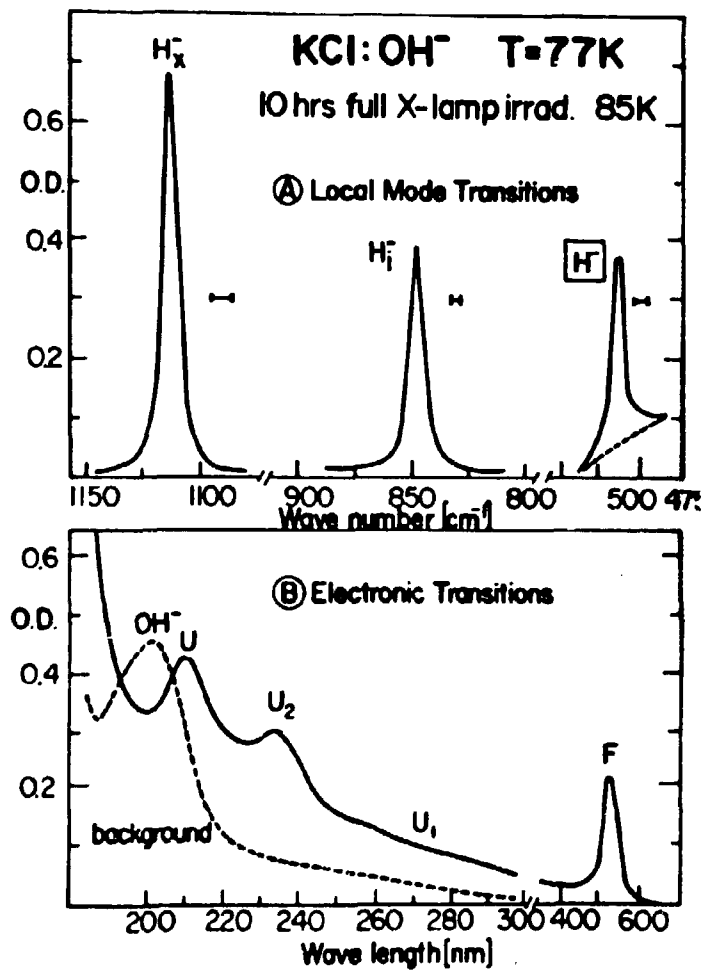A – KCI:OH⁻ system.

B – KCI:OH⁻ + Na⁺ system

Figure 3 A — Hydrogen centers local mode transitions after 10 hours of full Xenon lamp irradiation at 85K (measured at 77K).
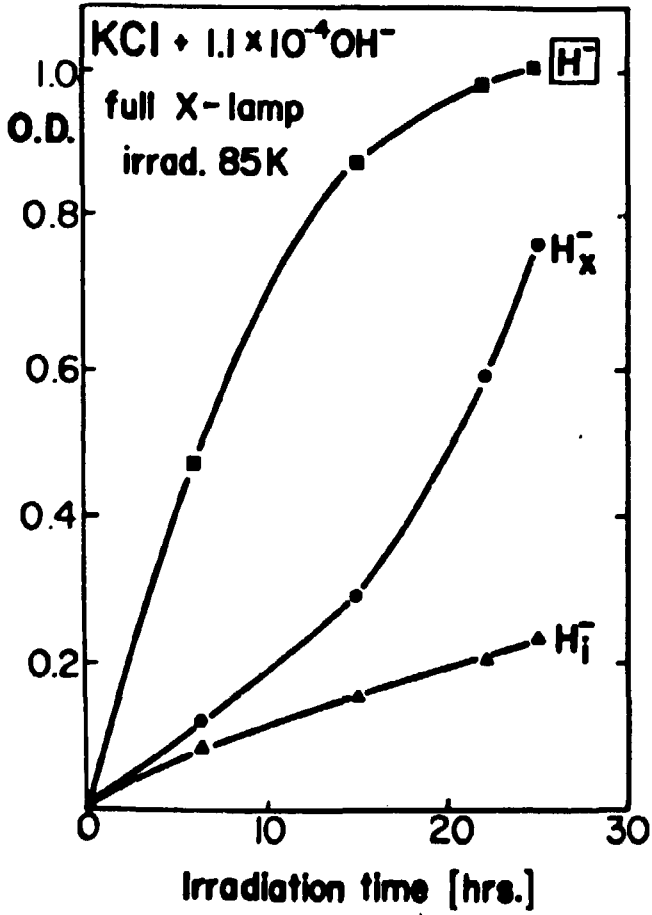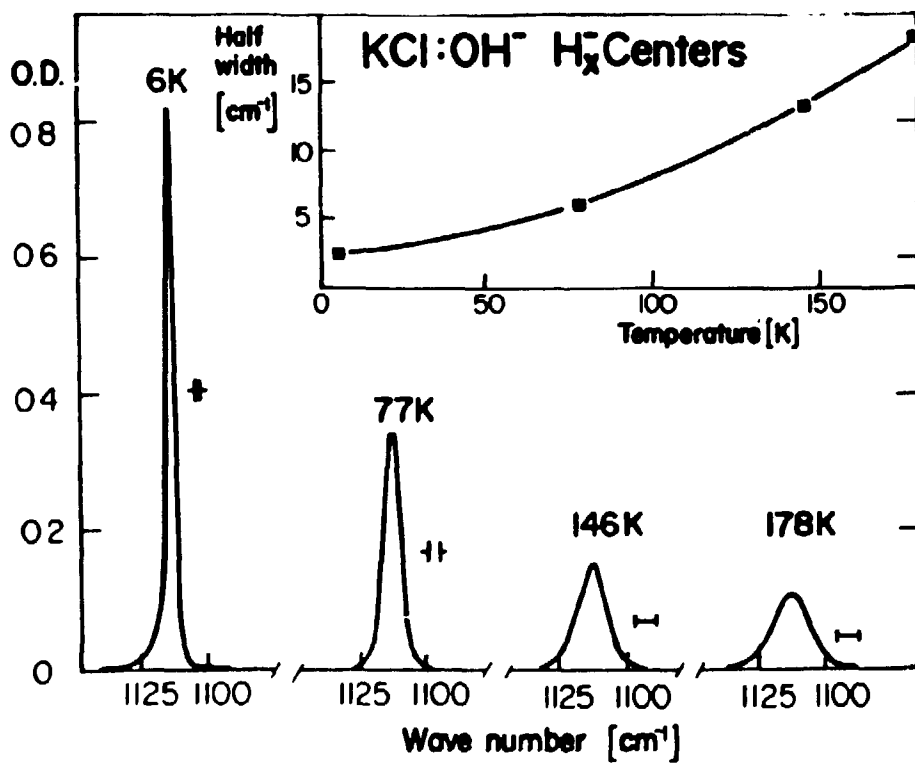
B – The respective UV spectra

Figure 4 — Plot of the local mode transitions of H⁻, H⁻ᵢ and H⁻ centers as a function of irradiation time under full Xenon lamp irradiation for a KCl:OH⁻ crystal with higher OH⁻ concentration.

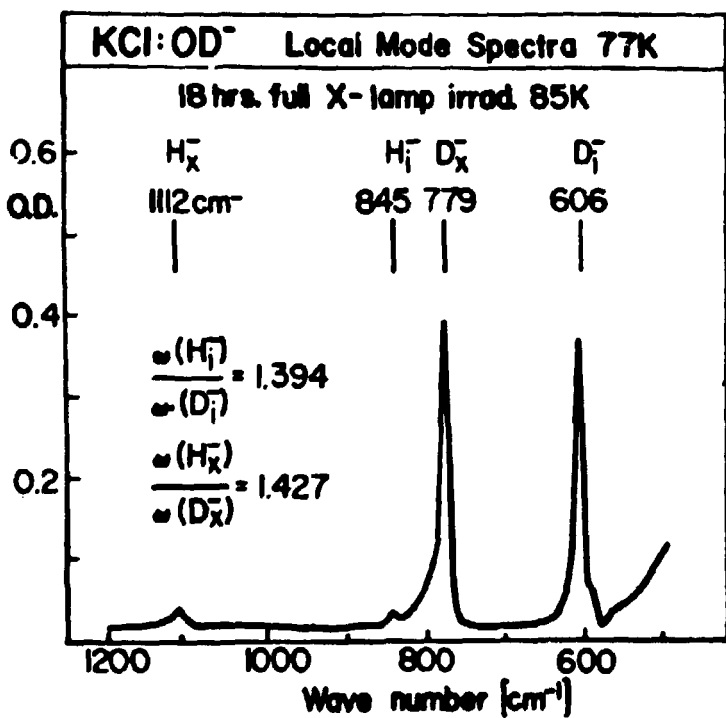**Figure 8** – *Temperature dependence of the spectral shape and halfwidth of the H_x local mode transition*

Figure 6 — Isotope shift effects of the H_x^- and H_i^- in a KCl:OD⁻ crystal after full Xenon lamp irradiation at 85K (measured at 77K).

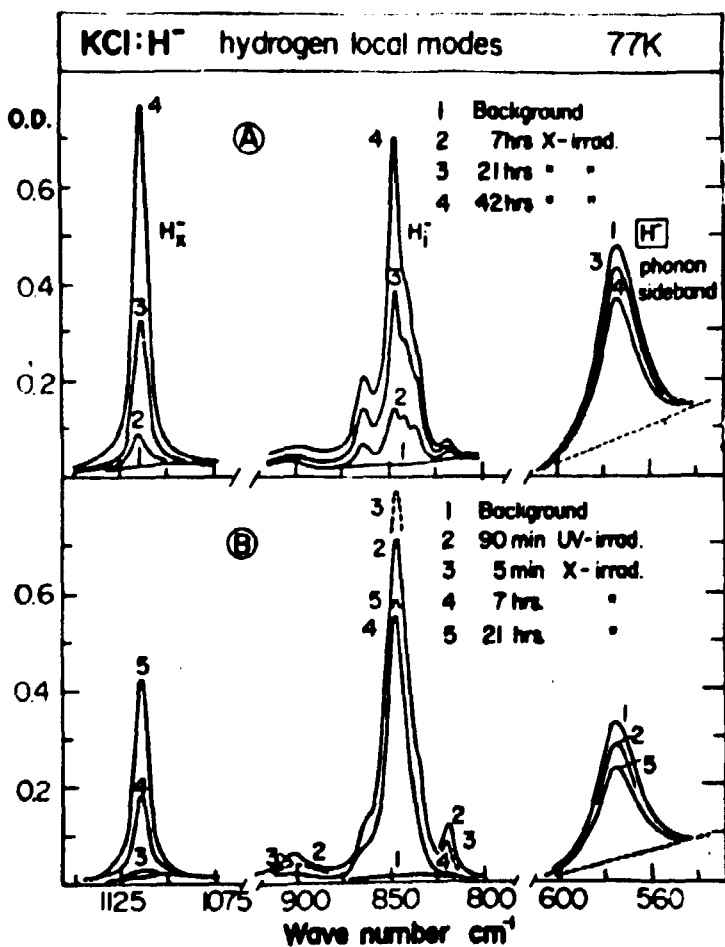Figure 7 A — Formation of H_x^- and H_i^- (of different spatial correlations) centers in a KCl + 5.6 x 10^{-5} H^- sample under X-rays irradiation at 77K.

B — The same as above but after a previous UV irradiation, producing H^- → H_i^- conversion.
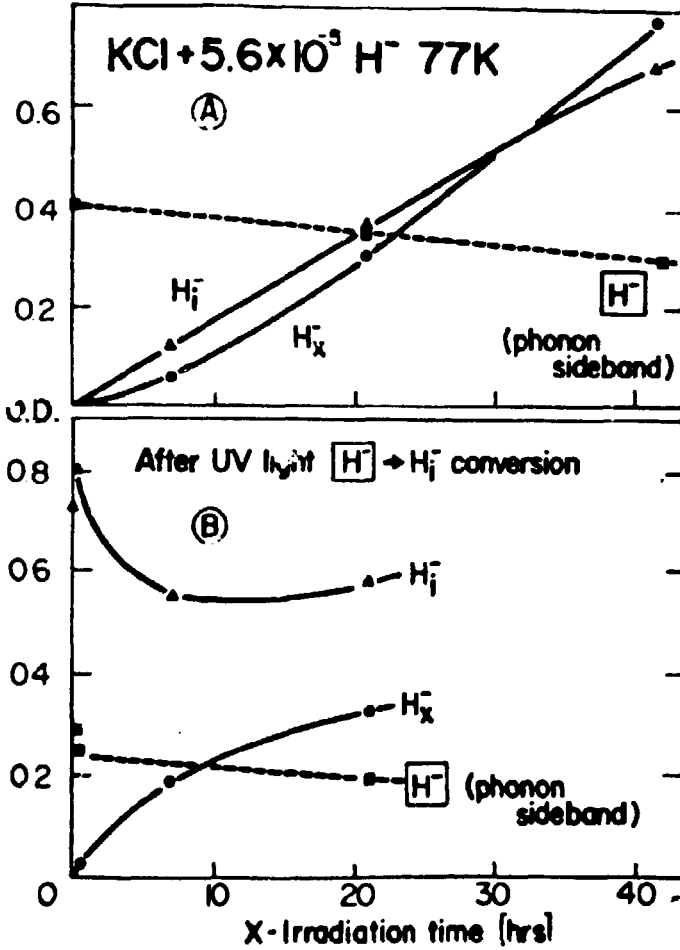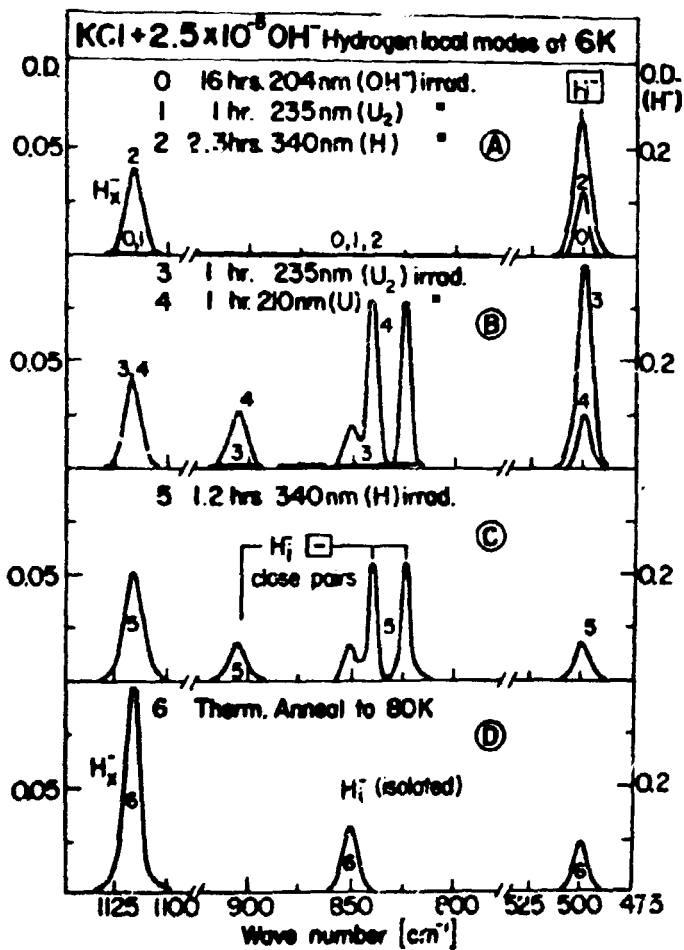
Figure 8 A – Increase of H_x^- and H_i^- (uncorrelated ones) as a function of X irradiation time. The consumption of H^- centers is monitored by the phonon sideband of the H^- local mode.

B – The same as above but after the previous UV irradiation. All data are taken from the spectral measurements in Figure 19

KCl + 2.5 x 10^{-5} OH$^-$ Hydrogen local modes at 6K

0.D.   0   16 hrs. 204 nm (OH$^-$) irrad.   O.D.
            1   1 hr. 235 nm (U$_2$)   ·   (H$^-$)
0.05   2   2.3 hrs. 340 nm (H)   ·   Ⓐ   H$^-$
        H$_x^-$ 0.2
            2   2
        0,1   0,1,2   0,1

            3   1 hr. 235 nm (U$_2$) irrad.   3
            4   1 hr. 210 nm (U)   ·   Ⓑ
                                              4
0.05   3,4   0.2
            4   3   4
            3   3   3

            5   1.2 hrs 340 nm (H) irrad.   Ⓒ
            H$_i^-$ ⊟
            close pairs
0.05   5   5   5   5   0.2

            6   Therm. Anneal to 80K   Ⓓ
        H$_x^-$ H$_i^-$ (isolated)
0.05   6   0.2
                                  6   6

1125 1100   900   850   800   525 500 475
Wave number [cm^{-1}]

Figure 9 — Local mode transitions of H$^-$, H$_i^-$ and H$_x^-$ under six different subsequent monochromatic irradiations at 6K (steps 0 → 5), and a final thermal annealing to 80K (step 6).
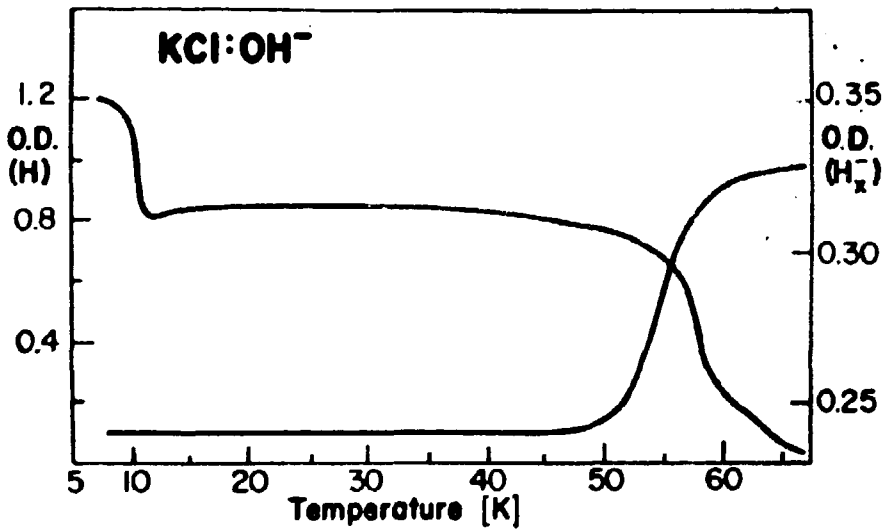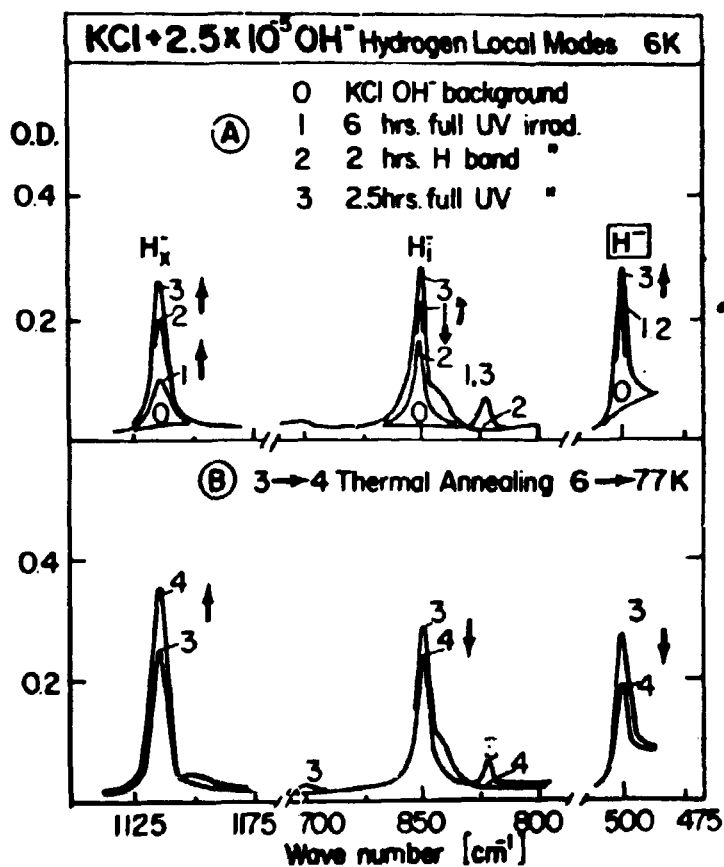
Figure 10 — H center decay and H_x^- build up curves vs. temperature. This measurement corresponds to the experiment shown in Figure 21D.

Figure 11 — Production of hydrogen centers in KCl:OH⁻ at 6K under undispersed light (broad band interference filter + Xenon lamp).

A — Step 1. Formation of H⁻, H_a^- (different correlations) and H_a^- centers under full UV irradiation. Step 2. H_a^- formation and H_i^- destruction under H band (Cl^0_i crowdion) light. Step 3. Repetition of Step 1.

B — H_a^- production after a thermal annealing process to 77K. K_i^- and H⁻ centers decrease after this treatment.
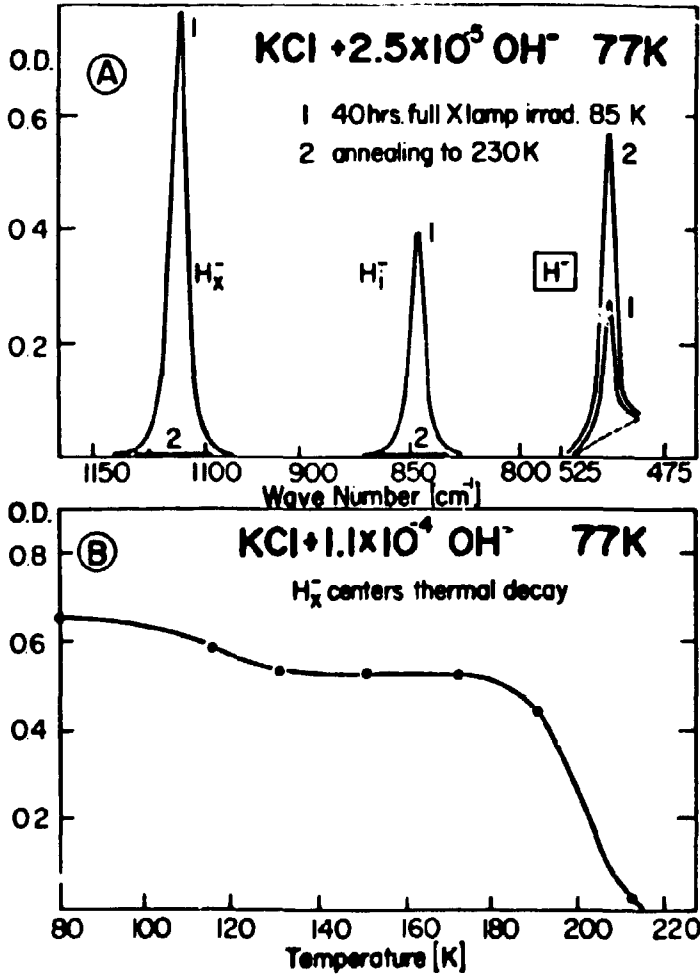
Figure 12 A — H_x^-, H_i^- and H^- centers local mode transitions before and after pulse annealing to 240K.

B — H_x^- center annealing curve at LNT taken under a pulse annealing procedure.
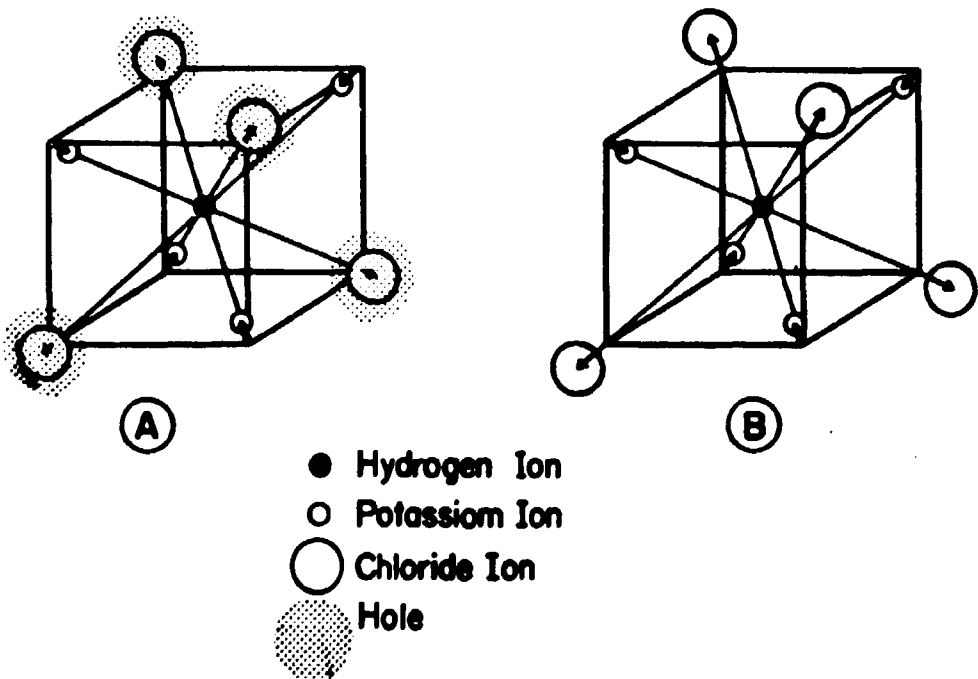
Figure 13 — Structural model of the H_a^- center (A) and the H_i^- center (B) with indication of the shifts in position of the surrounding anions and cations due to electrostatic interaction with the interstitial hydrogen ion.

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