Hydrogen defects from uv photodissociation of OH⁻ centers in alkali halides

Spero Penha Morato* and Fritz Lüty

Physics Department, .University of Utah, Salt Lake City, Utah 84112

(Received 22 January 1980)

A systematic investigation of the uv-light-induced photodissociation of substitutional OH⁻ defects in KCl has been performed in the whole temperature range between 4 and 300 K. The primary and secondary processes and their reaction products (O⁻, U_2, U, and H centers) are well understood and accounted for up to the point when the H center (Cl_2^- crowdion) becomes thermally mobile and reactive, leading to an unexplained loss of hydrogen defects. A detailed study of the related local-mode spectra in the infrared identifies this missing hydrogen by a new local-mode absorption band (tested in KCl, KBr, KI, and RbBr). Studies of the formation-kinetics of this new H_x^- defect show that it is produced by the reaction of mobile Cl_2^- crowdions with H⁻ defects. The same H_x^- centers can be produced by low-temperature x irradiation of KCl:H⁻ crystals. From these studies it becomes evident that the H_x^- defect is composed from the same electronic and ionic ingredients as the U_2 center, thus constituting an alternative stable configuration for this defect with completely different electronic and ionic structure. Among the possible structural models which are discussed, a mixed (H-Cl)⁻ dumbbell model appears to be the most likely one.

I. INTRODUCTION: HYDROGEN DEFECTS IN ALKALI-HALIDES

Similarly to other solid-state materials such as metals, ionic crystals have been extensively used to study hydrogen (and deuterium) defects under various conditions of temperature, irradiation, and chemical treatment. The simple electronic structure of hydrogen offers the possibility for an eventual full theoretical treatment and understanding of the static and dynamic properties of these fundamental lattice defects, while the small hydrogen mass makes these defects attractive candidates for quantum (tunneling) effects in their motional behavior.

The transparent, cubic single crystals of the alkali halides are particularly suitable for studies with spectroscopic methods because of the following:

(a) most hydrogen defects give rise to characteristic absorption bands (due to *electronic excitation*) in the transparent uv range of the host,

(b) charged hydrogen defects give rise to *local-mode absorptions* in the transparent ir range (due to their small mass compared to that of lattice ions), and

(c) hydrogen defects with unpaired spin can be studied in detail by *electron paramagnetic resonance* (EPR), *electron-nuclear double resonance* (ENDOR), *and magneto-optical techniques*.

For the study of hydrogen defects in alkali halides, two basic approaches have been followed experimentally.

(1) Crystals containing *substitutional* H⁻ *defects* (U centers) have been used as the starting material to produce various hydrogen defects by irradiation or thermal treatments. U centers are characterized by a strong structureless electronic absorption band in the uv (at 214 nm in KCl) and a narrow absorption line in the ir due to a localized vibration of the hydrogen ion [at 502 cm⁻¹ in KCl (Ref. 1)]. uv light irradiation into the U-band absorption *at low temperatures* transfers the H⁻ ion from its substitutional to an interstitial site (U_1 center) with an empty vacancy (α center) left at the original site.[2] This process can be monitored by the spectral conversion of both the electronic absorptions in the uv ($U \to U_1 + \alpha$ bands[3]) and the local-mode absorptions in the ir range.[4] Subsequent prolonged broad-band irradiation in the uv will excite the U_1 absorption of the H_i^- ion and can lead to its ionization and transfer of the electron back to the anion vacancy.[2] These primary and secondary processes can be represented by the following reactions:

$$[H^-] + h\nu \to [\,-\,] + H_i^-, \tag{1}$$

$$[\,-\,] + H_i^- + h\nu \to [e^-] + H_i^0. \tag{2}$$
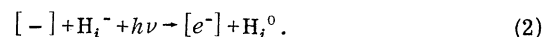
Here and in the following a bracket [H⁻] indicates a substitutional site and a lower index i (H_i^-) denotes an interstitial position. Besides these three hydrogen configurations (H⁻, H_i^-, and H_i^0), a fourth hydrogen defect of high symmetry, a neutral hydrogen atom H⁰ on an anion site (U_3 center), has been detected in small quantities by EPR and ENDOR techniques.[5]

Crystals with [H⁻] defects, when irradiated with uv light[6] or x rays[7] *at high temperatures* ($T > 150$ K), form, with increasing efficiency towards higher temperatures, F centers and interstitial hydrogen atoms. The latter recombine immediately to interstitial H_2 molecules[2]:

$$2[H^-] + h\nu + kT \to 2[e^-] + (H_2)_i. \tag{3}$$
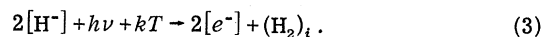
Besides producing these "fundamental" hydrogen defects, aggregation of hydrogen to other impurities can be achieved, too. Association of [H$^-$] defects into pairs,[8] to monovalent[9] (Na$^+$ or Li$^+$) impurities, and to F centers[10] can be obtained and identified by characteristic splittings of the local-mode absorption in these low-symmetry configurations.

(2) A second approach to produce various hydrogen centers in alkali halides is to start from *crystals doped with* OH$^-$ *ions*. As shown first by Kerkhoff,[11] uv-light excitation into the electronic transition of the OH$^-$ defect gives rise at low temperatures to a photodissociation process,

$$[OH^-] + h\nu \rightarrow [O^-] + H_i^{\,0}, \tag{4}$$

in which neutral interstitial hydrogen atoms (U_2 centers) and, most likely, substitutional O$^-$ defects are formed. While the presence of the U_2 centers is well secured by optical,[12] EPR, and ENDOR[13] measurements, the presence of negative oxygen defects from reaction (4) could never be verified by magnetic resonance.

In spite of this latter unsolved problem, the basic validity of the primary photoreaction (4) is generally accepted (and reconfirmed in this work). The quantum efficiency of the photodissociation process is found to be temperature independent and rather high at low temperatures. This indicates the possible presence of an antibonding excited state of the OH$^-$ defect, which causes (after optical excitation) a dissociation of the diatomic molecule without the need of thermal activation. It can be assumed that this fundamental photodissociation process is present with similar efficiency at all temperatures, and that the observed differences in the photochemistry are caused by differences in the *stability, mobility, and secondary optical excitations of the reaction products formed*. It is the aim of this work to study and clarify, over a wide range of temperatures, the reaction products and secondary processes initiated by the primary photodissociation process equation (4). As a similar primary process is possible in other alkali halides and in crystals with SH$^-$, SeH$^-$, and TeH$^-$ defects,[14-16] our study (done mostly with KCl:OH$^-$) may have model character for many crystal-defect systems.

II. EXPERIMENTAL PROCEDURES

The optical experiments were carried out with an He optical cryostat provided with four exchangeable uv and ir windows which permitted experiments using parallel and crossed optical beams together with the possibility of exchanging windows according to the specific spectral requirements of the experiment. To irradiate our samples with x rays at low temperatures, the crystal was provided with a fifth aluminum window at 45°, bisecting the perpendicular optical paths.

The KCl crystals were grown from the melt under a controlled argon-gas atmosphere in the Utah Crystal Growth Laboratory, using ultrapure grade material. Some ultrapure material was subject to pretreatment with HCl at high temperatures to eliminate as much as possible traces of OH$^-$ or oxygen impurities. In other crystals, KOH was intentionally added to the melt in controlled amounts in the range of 10^{-4} to 10^{-3} mole parts to dope the crystal with the desired OH$^-$ content. The samples were cleaved from the middle of the block to avoid possibly contaminated surface sections.

To color our samples additively, we employed the method described by Van Doorn[17] in which the F-center concentration of a desired value is obtained by controlling the vapor pressure of the metal vapor using an excess pressure of nitrogen gas. The hydrogenation of the additively colored samples consisted in the controlled diffusion of hydrogen into the crystal until all the F centers would react with hydrogen and produce substitutional hydrogen ions (U centers).

For undispersed uv-light irradiations, we used a 150-W xenon lamp from Hanovia #901C-11 mounted in a Bausch and Lomb lamp housing and equipped with a uv-grade quartz condenser lens system. For monochromatic irradiation in the uv region we used the xenon lamp mounting attached to a Bausch and Lomb grating monochromator. The bandpass used was approximately 20 nm. When it was necessary to obtain a fairly pure monochromatic irradiation, two monochromators were coupled in a tandem arrangement. The x-ray irradiation was always performed at 30 kV and 20 mA. Optical absorption measurements were carried out with the Cary 14 or Beckman ir 12 recording double-beam spectro-photometers.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Low-temperature photochemistry and the case of the missing hydrogen

Figure 1 summarizes the spectral changes characterizing the primary OH$^-$ photodissociation process: Monochromatic irradiation into the OH$^-$ band (shown at 6.5 and 78 K) reduces the OH$^-$ band with temperature-independent efficiency while increasing complimentary absorptions at lower and higher energies due to H$_i^{\,0}$ (U_2 centers) and O$^-$ centers, respectively. The difference in area between the OH$^-$ and U_2 bands reflects the dif-
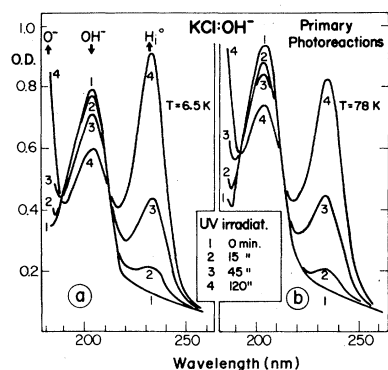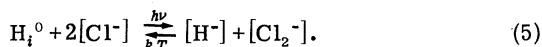
FIG. 1. uv-absorption spectra of KCl:OH⁻ before and after different times of irradiation with 204-nm light at 6.5 K (a) and 78 K (b). (O. D. is the optical density.)

ferent oscillator strength (0.13 and 0.33) of the two absorptions. As this photodissociation process is completely temperature independent below 100 K, we use in the following always, for economy, a liquid-nitrogen temperature (LNT) converted system as starting point for the further photochemistry.

In Fig. 2 we display the spectral changes (after the primary $OH^- \rightarrow U_2$ conversion) introduced by monochromatic light irradiation into the U_2 band (235 nm) at 6.5 K. In agreement with the detailed study of Kurz[18] we find a decrease of the U_2 band and a complimentary increase of the U and H bands, due to the formation of substitutional $[H^-]$ and trapped $[Cl_2^-]$ crowdions according to the reaction

$$H_i^0 + 2[Cl^-] \; \underset{kT}{\overset{h\nu}{\rightleftharpoons}} \; [H^-] + [Cl_2^-]. \qquad (5)$$

It is generally assumed that the U_2-band excitation of the H_i^0 center is due to a charge transfer transition, in which the hole bound at the interstitial H^- ion is transferred to the tetrahedron
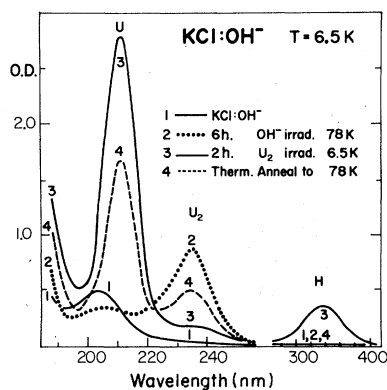

FIG. 2. uv-absorption spectra of KCl:OH⁻ before and after the indicated optical irradiation with OH⁻ and U_2-band light, and after pulse annealing to 78 K.

of four surrounding Cl⁻ ions. This excitation does *not* produce a radiative back process, but instead initiates and stabilizes the electronic and ionic rearrangements, found experimentally (Fig. 2) and described by reaction equation (5). The possible sequence of events, as suggested by Kurz,[18] is illustrated in Fig. 3. The optically induced transfer of the hole to the Cl⁻ ions produces a Jahn-Teller distortion of the Cl⁻ ions along ⟨110⟩ directions as indicated, localizing the hole more strongly at the Cl⁻ ions which approach each other and displacing the H⁻ ion towards the latter. The formed Cl_2^--crowdion configuration can apparently propagate in a ⟨110⟩ replacement sequence, becoming stabilized in the H-center dumbbell configuration.[19] (We avoid the notations "H center" due to its misleading confusion with hydrogen (H) defects, using instead "$[Cl_2^-]$ crowdion" for its chemical and structural characterization.)

It is reasonable to assume that the processes (a)–(d) in Fig. 3 are strongly influenced by the fact that due to local-mode vibration, the H atom can have at times sizable deviations from its central position in the Cl⁻ tetrahedron. Any incidental ⟨100⟩ deviation of the H atom during optical excitation will favor directly the charge transfer to the two nearest Cl⁻ ions [process (c) in Fig. 3], while any ⟨110⟩ deviation from the central place will introduce the asymmetry necessary to produce a preferred direction for the ⟨110⟩ replacement sequence.

Figure 4 shows the measured changes in the height of the U_2, H, and U bands as a function of monochromatic U_2-band irradiation at 6 K. The obtained straight-line dependences between formed reaction products $[H^-]$ and $[Cl_2^-]$ and destroyed H_i^0 centers are in agreement with the reaction
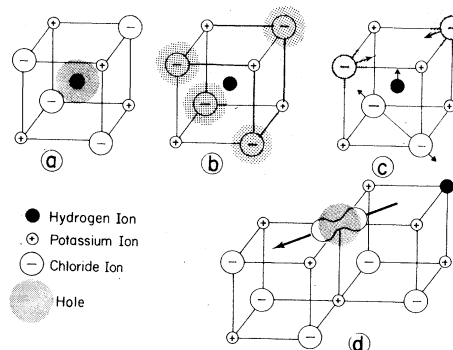

FIG. 3. Illustration of the electronic and ionic configurations and processes involved in the optical H_i^0-center destruction: (a) H_i^0 ground state, (b) H_i^0-center relaxed excited state after charge transfer of hole, (c) subsequent Jahn-Teller distortion, and (d) formation of $[H^-]$ center and $[Cl_2^-]$ crowdion.
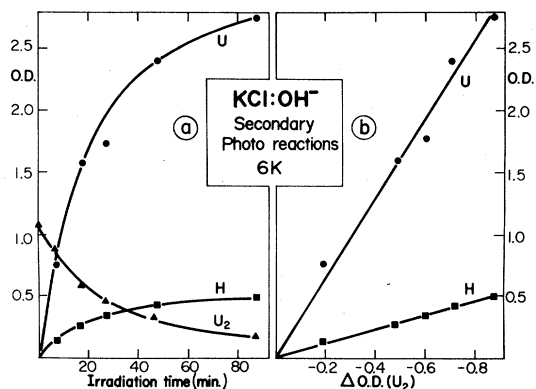
FIG. 4. Photodecomposition of H_i^0 (U_2) centers at 6 K. (a) Decrease of the U_2-band absorption and increase of U- and H-band absorption as a function of irradiation time (monochromatic 235-nm light). (b) U- and H-band increase plotted as a function of the U_2-band decrease, yielding linear interrelations.

equation (5), yielding together with bandwidths the relative oscillator strengths of the U_2, U, and H-band absorptions. It should be noted that the U band produced in this way has a larger width compared to its normal shape in KCl:H^- crystals, apparently due to a close spacing and interaction between the [H^-] center and [Cl_2^-] crowdions.

The reaction process in Eq. (5) can be reversed by heating the crystal to temperatures above 50 K where the [Cl_2^-] becomes thermally mobile. After annealing to 78 K (and the expected total destruction of the H-band absorption of the [Cl_2^-] centers), we find, however, that the *reaction in Eq. (5) has been only partially reversed*: Only a fraction of the U band has been destroyed by the thermal annealing (Fig. 2, curve 4). Evidently the thermally destabilized [Cl_2^-] must have followed another process and formed a reaction product other than the ones described by the back reaction in Eq. (5).

This problem becomes more evident if the optical U_2-center decomposition is performed directly at LNT, where the [Cl_2^-] is unstable and no H-band absorption can be formed. In spite of this fact, one finds, similar to the results in Fig. 1 at liquid-helium temperature (LHeT), a decrease of the U_2 band and increase of the U band. Comparison of the reaction rates (Fig. 5) however, shows the following:

(a) The initial quantum efficiency for the optical H_i^0-center destruction is about ten times smaller than it was at LHeT.

(b) Although a linear relation between the U_2-band decrease and U-band increase is again observed, the ratio is different from the one obtained at LHeT.

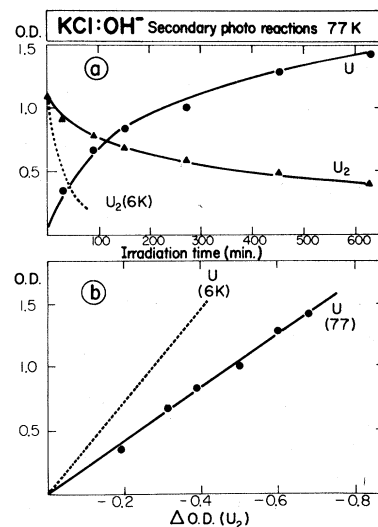Phenomenologically, point (a) shows that the

FIG. 5. Photodecomposition of U_2 centers at 77 K. (a) Decrease of the U_2-band absorption and increase of the U-band absorption. (The dashed line indicates the initial rate obtained at 6 K.) (b) U-band increase plotted as a function of the U_2-band decrease. (The dashed line indicates the same reaction at 6 K corrected for the broadening effect on the perturbed H^- centers.)

stability of the H_i^0 center against optical bleaching is considerably higher than at LHeT. If we assume that the initial photodestruction of the H_i^0 center produces the [Cl_2^-]-crowdion center (as it does at LHeT), this thermally unstable interstitial center may easily recombine and restore the initial H_i^0 center. This would account for the low efficiency of the H_i^0-center photodestruction.

Still, in 10% of the U_2-band excitation cases (compared to LHeT), the H_i^0 photodestruction works and U centers *are* formed. This means that the mobile [Cl_2^-] crowdion *did* escape without recombination and must get trapped and stabilized at some unknown place, undetectable with uv and visible spectroscopy. The fact that in this process the $|\Delta U|:|\Delta U_2|$ ratio is different from the 1:1 ratio found at LHeT as indicated in (b) suggests that *hydrogen in some form may be involved in the stabilization and trapping of the* [Cl_2^-] *crowdion.*

The precondition for this line of argument is the assumption that the photoexcitation of the H_i^0 center at LNT leads, as in the LHeT case, primarily to the formation of a [Cl_2^-] crowdion, even if this defect does not remain thermally stable and therefore is not detectable by the H band. This assumption was experimentally tested by supplying traps in the crystal which are able to stabilize the mobile [Cl_2^-] crowdions. It is known that Na^+ defects in KCl have this ability, trapping and stabilizing the [Cl_2^-] crowdions as "H_A centers"

up to 113 K in temperature.[20] We repeated the optical U_2-band destruction at LNT in a Na^+-doped crystal, obtaining the spectral results shown in Fig. 6. In contrast to the pure $KCl:OH^-$ crystal, we observe now the $[Cl_2^-]$ crowdions, trapped at Na^+ impurities, by the characteristic H_A absorption bands at 357 and 560 nm. This proves that photoexcitation of H_i^0 centers at LNT leads, as at LHeT, to the production of $[Cl_2^-]$ crowdions as described by Eq. (5). Owing to their thermal mobility, a large fraction of the $[Cl_2^-]$ crowdions recombine with the U centers, accounting for the low bleaching efficiency (Fig. 4). A part, however, of the $[Cl_2^-]$ crowdions escapes recombination and must produce a new reaction. The result in Fig. 5(b) shows clearly that compared to the one-to-one conversion $U_2 \rightarrow U$ at LHeT more H_i^0 defects have been consumed at 77 K to produce the same amount of $[H^-]$ defects. We therefore conclude that the *reaction of mobile* $[Cl_2^-]$ *crowdions with* $[H^-]$ *defects must form another reaction product* which does not give rise to any characteristic uv or visible absorption. In an attempt to identify this "invisible" reaction product, we set up infrared experiments.

B. Local-mode spectroscopy and the new H_x^- defect

Figure 7 shows the effect of various spectral irradiations at 77 K, measured in terms of the strengths of characteristic absorptions in both the ultraviolet and infrared range. We started with the primary OH^- photodecomposition by 204-nm light irradiation (like in Fig. 1), producing in the uv range the bleaching of the OH^- band and development of the U_2 band. In the ir range no significant spectral changes can be observed at this stage, as expected. The OH^-
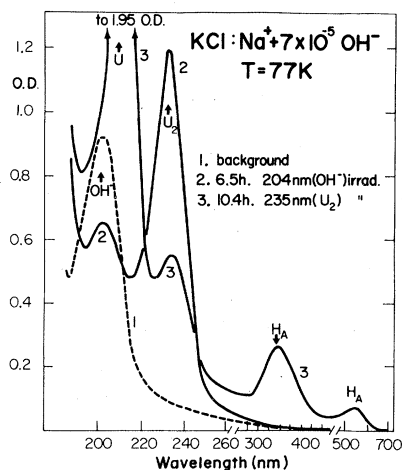
stretching vibration at 2.7 μm is too weak to be detectable for the low-OH^- doping used, and the neutral H_i^0 interstitial does not give rise to an optically active local mode. In the next step we photodestroyed H_i^0 centers, reproducing our former uv spectral results (Fig. 2). In this irradiation stage, 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 to be ir active.

Proceeding with the sequence of spectral irradiations in Fig. 7, we illuminated in the third stage with U-band light, producing the well-known $[H^-] \rightarrow H_i^-$ conversion. This step basically did not change the optical density of the H_x^- center. As expected, we observed in both ranges (ir and uv) the decrease of the H^- center (U band). Besides the increase of the H_i^- center, the U-band destruction is also responsible for the formation of some pairs of F and H_i^0 centers. The new H_x^- defect apparently does not participate in all these
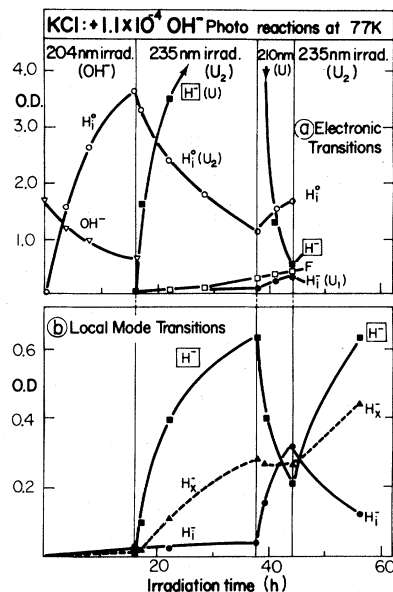

FIG. 6. uv-absorption spectra of a $KCl:OH^-:Na^+$ crystal after primary (OH^-) and secondary (U_2) photodecomposition at 77 K.

FIG. 7. (a) Electronic absorption bands as a function of irradiation time for a sequence of monochromatic irradiations in a $KCl:OH^-$ crystal (thickness ~ 0.5 mm) at LNT. (b) Local-mode transitions in the ir for the same sequence of irradiations as in (a) (crystal thickness ~ 8.0 mm).

transformations.

A repeated U_2-band irradiation produces again, as in the second step, an increase of both the H_x^- and H^- local-mode absorption. In contrast to these results in Fig. 7, a similar set of experiments with a KCl:Na^+ crystal did not produce a trace of the H_x^- local-mode band (but showed instead the H_A-band absorption in the uv, as mentioned before—Fig. 6).

Employing instead of the subsequent monochromatic uv irradiations of Fig. 7 a full undispersed irradiation from a xenon lamp produces the same reaction products in some form of dynamical equilibrium. Figure 8 shows the results after 10 hours of irradiation at 85 K: the three local-mode bands from [H^-], H_i^-, and H_x^- centers in the infrared, and the U_1, U_2, and U-band absorption (plus a small amount of F centers) in the uv–visible range. In terms of total local-mode absorption strength, the H_x^- defect is the most prominent reaction product of this photodecomposition process; it lacks, however, a characteristic electronic absorption in the uv–visible range. A repetition of the irradiation in a KCl:OH^-:Na^+ crystal yields the same result as in Fig. 8. The intense light irradiations into the H_A band bleaches out (as we tested with monochromatic light) this absorption: Optical destabilization of the trapped [Cl_2^-] crowdions therefore leads to the same H_x^- defects as in the KCl:OH^- crystal without traps.

Figure 9 shows the infrared spectral results after an undispersed xenon-lamp irradiation in a KCl:OD^- crystal. Both the H_i^- and H_x^- absorp-

FIG. 9. Local-mode spectrum of KCl:OD^- crystal at 77 K after undispersed xenon-lamp irradiation at 85 K.

tions are found to be shifted to lower energies by a factor close to $\sqrt{2}$ (while the D^- local mode is out of scale). This clearly identifies the H_x^- absorption as a *highly localized mode of charged hydrogen*. The temperature dependence of the H_x^- transition, displayed in Fig. 10, shows a gradual broadening of the band to high temperatures and the absence of any substructure at lowest temperature within the resolution limit (~ 1.5 cm^{-1}). Exploratory experiments with KBr:OH^-, KI:OH^-, and RbBr:OH^- crystals after undispersed xenon-lamp irradiation at 80 K showed that, in addition to [H^-] local modes, the same type of new H_x^- absorption appears in these crystals (at 1095 cm^{-1} in KBr, at 882 cm^{-1} in KI, and at 1021 cm^{-1} in RbBr). This demonstrates the general nature of the OH^- photodecomposition process and its prominent H_x^- reaction product in various hosts. Moreover, we tested the same process in KCl:SH^- crystals, for which it is known from previous work[15] that a photodecomposition (similar to the OH^- case) into S^- and H_i^0 defects is possible. As the result of full xenon-lamp irradiation in KCl:SH^-, the same
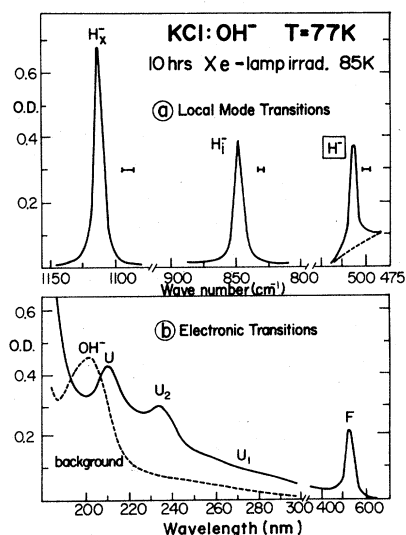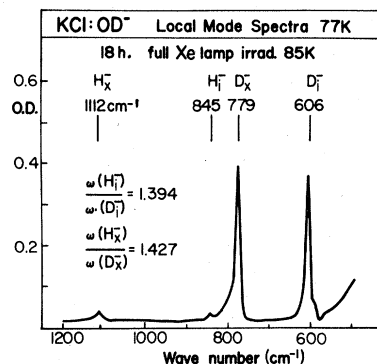

FIG. 8. Absorption spectra of a KCl:OH^- crystal after 10 hours of undispersed xenon-lamp irradiation at 85 K, measured (at 77 K) in the infrared (a) and uv–visible (b) range.
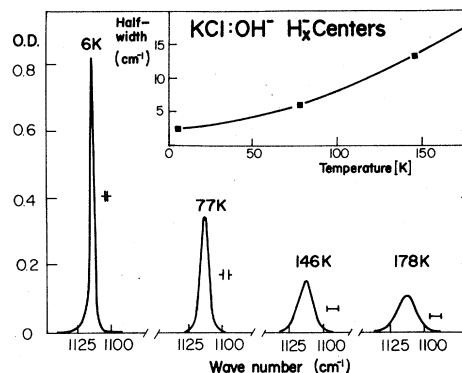

FIG. 10. Temperature dependence of the spectral shape and halfwidth of the H_x^- local-mode absorption.

H_x^- band was formed as in KCl:OH⁻ crystals.
This experiment clearly rejects the concept that
the other partners of the primary photodecompo-
sition (oxygen and sulfur) are involved in the de-
fect structure of the H_x^- center.

This latter point was confirmed by a further
experiment in which we tested the general idea
that the H_x^- defect is formed by the reaction of
mobile $[Cl_2^-]$ crowdions with hydrogen defects.
As $[Cl_2^-]$ crowdions are effectively produced by
high-energy radiation at low temperatures,[21] we
x-irradiated hydrogenated pure KCl crystals with
5.6×10^{-5} [H⁻] defects at 78 K and monitored their
local-mode absorption in the infrared. Figure
11(a) shows the result as a function of x-ray ex-
posure. The [H⁻] defects (initially present alone)
decay gradually under x irradiation, as monitored
by the weak phonon-side band of the (out-of-scale)
[H⁻] local-mode band. Parallel to this, the for-
mation of both H_i^- and H_x^- local-mode absorptions
is observed, the formation rate of the latter be-
coming stronger with increasing x-ray exposure.
In a separate experiment [Fig. 11(b)], the KCl:H⁻
crystal was first exposed to uv-light irradiation,
which produces optically a strong conversion of
substitutional into interstitial H⁻ defects.[2-4] Sub-
sequent exposure to x irradiation leads with high
efficiency to a conversion of the optically pro-
duced H_i^- defects into H_x^- centers. Apparently
the mobile $[Cl_2^-]$ crowdions react much more
effectively with the interstitial H⁻ defects com-
pared to the substitutional ones.

In all these local-mode experiments so far we
have used a temperature $T > 50$ K, where the

$[Cl_2^-]$ crowdions are *mobile right after their
creation* and thus form the H_x^- defects almost
instantaneously. A better and separated con-
trol over the various reactions should be achie-
vable at lower temperatures in the range where
the $[Cl_2^-]$ crowdions are stable. Figure 12 shows
the local-mode results in a KCl:OH⁻ crystal after
various treatments at 6 K. In an initial step, the
primary OH⁻ photodecomposition into U_2 centers
was achieved by 16 hours of monochromatic 204-
nm irradiation at LNT. Cooled to 6 K, the cry-
stal shows, as expected, no local-mode absorp-
tion (similar to the result in Fig. 7) at this stage
0. After subsequent U_2-band irradiation at 6 K
we observe that the H⁻ local mode was built up,
as expected from previous experiments (stage 1).
In contrast to the corresponding experiment at
LNT (Fig. 7), we observe at this stage *no trace
of an H_x^- formation*. The "self-trapping" of the
$[Cl_2^-]$ crowdions as stable H centers prevents the
formation of H_x^- defects. If our line of argument
is correct, the H_x^- should, however, be formed
if we mobilize the self-trapped $[Cl_2^-]$ crowdions
in some way. One way to achieve this is the opti-
cal excitation in the electronic transition (H band)
of the $[Cl_2^-]$ crowdion, which leads to an optically
stimulated motion of the defect. If we shine mono-
chromatic light into the H band (stage 2 in Fig. 12),
we indeed observe the appearance of the H_x^- local-
mode band together with 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
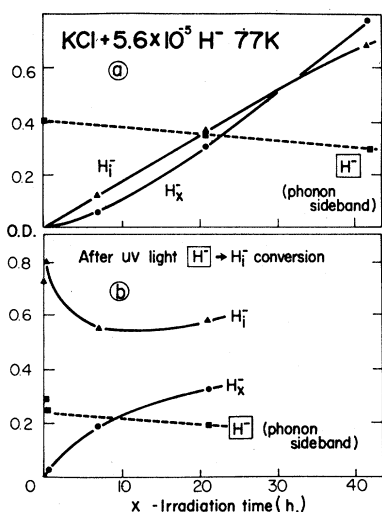the reaction of "optically mobilized" $[Cl_2^-]$ crow-

FIG. 11. KCl:H⁻ crystal under x irradiation at 77 K.
(a) Increase of H_x^- and H_i^- local-mode absorption as a
function of x-irradiation time. (b) Same as (a), but after
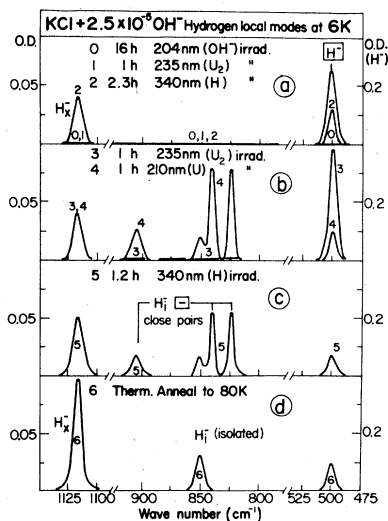previous uv irradiation (H⁻ → H_i^- conversion).

FIG. 12. Local-mode absorption of H⁻, H_i^- and H_x^-
defects before and after different monochromatic irradi-
ations at 6 K (stages 0–5), and after thermal annealing
to 80 K (stage 6).

dions with [H⁻] defects.

A further irradiation to the U_2 band (stage 3 in Fig. 12) proceeds with the $H_i^0 \rightarrow [H^-] + [Cl_2^-]$ formation as in stage 1 without further H_x^- formation. A subsequent monochromatic irradiation in the U band is found to build up mainly the local mode of $H_i^-/[-]$ close pairs[4] (stage 4, Fig. 12) with the corresponding decrease of the [H⁻] absorption. Now that we have two kinds of hydrogen centers competing as trapping sites, we again optically bleach the H band and observe the 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⁻] mode. Apparently when both [H⁻] and $H_i^-/[-]$ pairs are offered, the latter are much more effective for the H_x^- formation, exactly what we observed in the x-ray experiment with the KCl:H⁻ crystals at LNT [Fig. 11(b)].

The second possibility for mobilizing the $[Cl_2^-]$ crowdions after their optical creation at LHeT is a *thermal annealing process* into the temperature range of their thermal instability ($T > 55$ K). This process was performed as stage 6 in Fig. 12(d). 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[4] only at $T > 90$ K), 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 stage 6.) Thus again we can conclude that thermally mobilized $[Cl_2^-]$ crowdions form H_x^- centers by reacting preferentially with $H_i^-/[-]$ close pairs.

The involvement of the $[Cl_2^-]$ in the H_x^- formation is conclusively demonstrated in Fig. 13 in which we monitor the absorption of the $[Cl_2^-]$ crowdions (H band) and the H_x^- local-mode absorption during the thermal annealing process. The correspondence of the thermal destruction
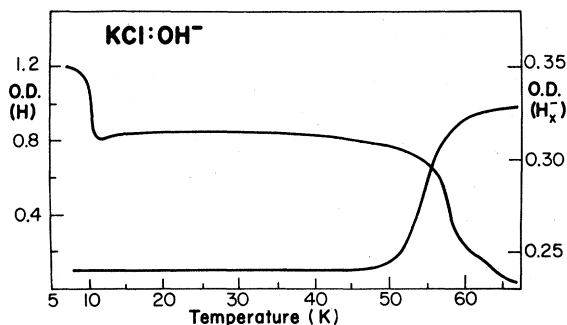
of the $[Cl_2^-]$ centers (around 55 K) to the increase of the H_x^- absorption is clearly demonstrated (the change in the H-band absorption at 10 K is caused by thermal reorientation of the $[Cl_2^-]$ crowdions).

An alternative experiment at 6 K, which employed in stage 1 undispersed light from the xenon lamp, produced immediately the local-mode bands of all three hydrogen defects [H⁻], H_i^-, and H_x^-. Simultaneous bleaching in the U-band and H-band absorption explains this behavior readily.

Finally, after these detailed studies on the kinetics of formation of H_x^- defects, we tested their thermal stability and the possible reaction products of their thermal destruction. Measurements of the H_x^- local-mode absorption after pulse annealing to various higher temperatures shows that its thermal decay occurs in the range 180–210 K (Fig. 14). This annealing behavior is very close to the $H_i^- \rightarrow [H^-]$ thermal decay of H_i^- interstitials,[4] and we indeed observe together with the H_x^- extinction the thermal destruction of the H_i^- local-mode absorption. The parallel increase of the [H⁻] local mode is fully accounted for by the recombination of thermally unstable H_i^- ions into vacancies, forming the [H⁻] defects. *Evidently the thermal destruction of the H_x^- local mode does not lead to the formation of substitutional H⁻ defects.*

C. Conclusions and possible structural model of the H_x^- center

We have shown by a large variety of experiments that two ingredients are necessary for the
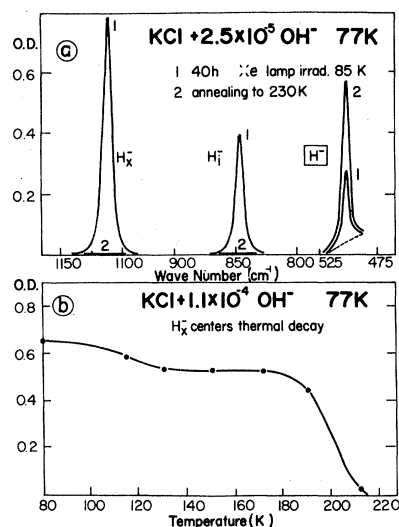

FIG. 13. Decay of the H band and buildup of the H_x^- local-mode absorption as a function of temperature.

FIG. 14. (a) H_x^-, H_i^- local-mode absorptions before and after pulse annealing to 240 K. (b) Pulse-annealing curve of the H_x^- local mode, measured at 77 K.

H_x^- formation:

(a) H_x^- defects are formed *only* when mobile $[Cl_2^-]$ crowdions are present. This can be achieved either *instantaneously* by optical or x-ray irradiation above 55 K in the range of $[Cl_2^-]$ thermal mobility, or in a *delayed way* after low-temperature irradiation by destabilizing self-trapped $[Cl_2^-]$ crowdions (H centers) using optical excitation or thermal annealing.

(b) H_x^- defects are formed *only* when H^- defects are present, either in substitutional or interstitial form. If H^- is present in both forms, the H_i^- defects are much more effective for H_x^- production.

The infrared absorption properties characterize the H_x^- defect as a charged hydrogen atom with a highly localized vibration and an eigenfrequency ~30% higher than that of the H_i^- interstitial. The unsplit local mode seems to indicate a local site of high symmetry. In the destruction of the H_x^- defect, no other recognizable hydrogen absorption (as from $[H^-]$ defects) is formed. The variation of the H_x^- local-mode frequencies among the four investigated host crystals follows an Ivey-law trend with lattice parameter, similar to the one for $[H^-]$ and H_i^- local modes (Fig. 15). A structural model must be able to satisfy and integrate all these static and dynamic experimental features. The first requirement for a model is that it explain the formation of the center from the building blocks involved, the $[Cl_2^-]$ crowdion, the H^- ion, and an anion vacancy (the two latter units either separated as a Frenkel pair or united as a $[H^-]$

FIG. 15. Summary of the known wave-number values of H_x^-, $[H^-]$, and H_i^- local-mode absorptions in alkali halides, plotted in double logarithmic scale against the lattice parameter.

defect). Compared to a perfect lattice (with one negative ion per anion site), the summation over these building blocks constitutes an *excess of one anion* (H^- *or* Cl^-) *and one hole*. One possible configuration which accommodates the sum of these building blocks is the U_2 center, in which the H^- ion occupies an interstitial position and binds the excess hole. We therefore see that *in terms of the building blocks involved, the H_x^- defect is equivalent to the U_2 center.* After optical decomposition of the U_2 center into an $[H^-]$ defect and an escaped $[Cl_2^-]$ crowdion, the recombination of the mobile crowdion with the $[H^-]$ defect (or $H_i^-/[-]$ pair) apparently does *not* lead back into the U_2-center configuration, but into an *alternative arrangement of the electronic and ionic entities involved.* One requirement for this new H_x^- configuration is that the excess hole should not be bound solely to the H^- ion, because a charged hydrogen atom is needed to explain the H_x^- local mode. As there exists one excess ion in the total configuration we have, in principle, three possibilities for the location of the anions involved:

(A) the H^- ion occupies an interstitial position and the Cl^- ion a substitutional site,

(B) the required interstitialcy is shared by the H^- and Cl^- ion, and

(C) the H^- ion occupies a substitutional and the Cl^- ion an interstitial place.

Each part of this assumption leads to a possible H_x^- configuration which we will discuss as follows.

(A) If the H^- ion occupies the high-symmetry interstitial position without binding a hole, the hole could be distributed and bound equally by the four Cl^- ions surrounding the H^- interstitial [Fig. 16(a)]. This would create a site of high symmetry for the H_i^- in which the local mode would not split, as observed. The addition of a hole to the tetrahedron of Cl^- anions will reduce the electrostatic $Cl^- \leftrightarrow H^-$ repulsion and thus produce most likely a closer distance between the H_i^- and Cl^- 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 the local-mode frequency of the H_x^- defect to lie somewhat higher than that of the H_i^- defect, as it is observed.

In spite of this good qualitative agreement with the local-mode properties, there is a serious objection against this model (A): It is basically the configuration which is assumed to be the unrelaxed excited state of the U_2 center (see Fig. 3). The latter is believed to be responsible for the instability of the U_2 center after optical excitation and the ejection of the crowdion. It is extremely hard to understand how a similar con-
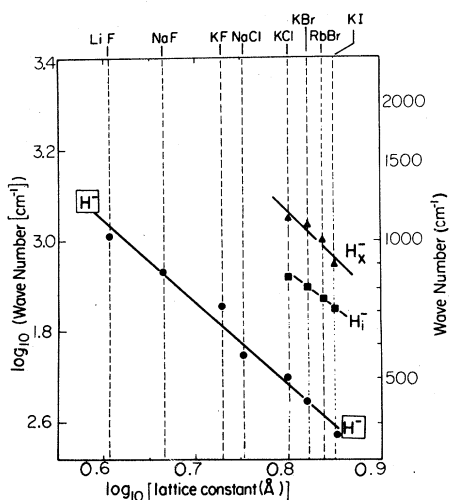
figuration could be a very stable one in the H_x^- case, producing neither the crowdion ejection nor a conversion process into the U_2-center ground state up to ~220 K. The only difference from the unrelaxed excited U_2 state could be the structure and spacing of the lattice cell around the interstitial hydrogen. For the unrelaxed excited U_2-center state, the ionic configuration of the surroundings is still in equilibrium with the U_2-center ground state, i.e., a hole at the interstitial hydrogen. For the hypothetical H_x^- configuration in Fig. 16(a), the ionic configuration will be in equilibrium with the hole being distributed over the Cl^--ion tetrahedron. This difference can surely produce a different stability in terms of electronic and ionic transitions from the two states. Still it is extremely hard to understand the perfect separation and absence of any conversion between the two alternative electronic and ionic configurations.

(B) The reaction of the mobile $[Cl_2^-]$ crowdion with the H^- could lead to a mixed crowdion $[HCl^-]$ which is stable in terms of ionic mobility or separation up to ~200 K [Fig. 16(b)]. The $[HCl^-]$ should not be considered in a state of real tight molecular binding, but in a dumbbell configuration at an anion site in which the equilibrium H–Cl distance is determined strongly by the lattice potential. Therefore the vibrational eigenfrequency of the HCl^- is *not* as high as that of an HCl molecule $[\nu(HCl) = 2886$ cm$^{-1}]$, but lies instead between this value for true molecular vibrations and typical values for H^- local modes. The biggest problem for this model lies in the observation of a *single unsplit local-mode line*. Unquestionably, the vibration of the hydrogen along the crowdion axis and perpendicular to it cannot
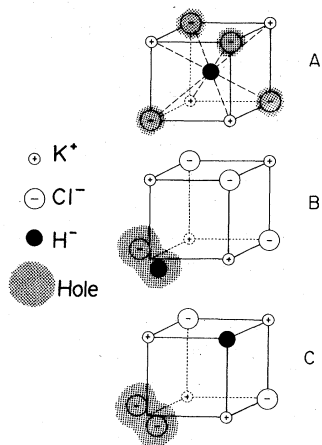

FIG. 16. Possibilities for structural models of the H_x^- center, which are compatible with the general chemical composition as derived from the formation kinetics.

have the same eigenfrequency and produce a single band. The difference in the vibrational potential could in fact be so large that we observe in the accessible spectral range only the linear hydrogen motion along the crowdion axis ("stretching motion of the HCl^- quasimolecule"). A vibration of the hydrogen perpendicular to this axis would correspond to a "hindered rotation of the HCl^- quasimolecule," the frequency of which could be low enough to lie outside of our investigated spectral range (i.e., $\nu < 450$ cm^{-1}). An experimental search for this possible lower lying hydrogen vibration could clarify this question and the validity of model (B).

(C) The reaction of the mobile $[Cl_2^-]$ crowdion with the $[H^-]$ defect could leave the H^- on its substitutional site and lead to a stabilization of the $[Cl_2^-]$ crowdion close to it [Fig. 16(c)]. Although this configuration satisfies the general building-block requirement, it is very unlikely in terms of its expected optical behavior: The $[Cl_2^-]$ crowdion, trapped near the substitutional H^- defect, could not produce a single local-mode band as observed, but should produce split local-mode bands with all frequencies rather close to the one of the normal $[H^-]$ defect. Similarly, the trapped $[Cl_2^-]$ crowdion should give rise to a perturbed electronic H-band transition, as it is observed for $[Cl_2^-]$ crowdions trapped at other point defects (such as the H_A band of the KCl:Na$^+$ case in Fig. 6). Owing to these adverse optical arguments we regard model (C) as very unlikely.

All three models, being identical in terms of the net chemical nature of the defect complex, can explain the observation that thermal destruction of the H_x^- defect does *not* produce any new local-mode absorption (in particular, no $[H^-]$ local modes). As, chemically speaking, both the H_x^- defect and the U_2 center consist of an excess neutral hydrogen atom, thermal destabilization can in principle always produce H_2 interstitial molecules which are optically invisible.

The case of the H_x^- and H_i^0 (U_2) centers (if our general considerations are correct) constitutes to our knowledge the *first example in ionic crystals in which the same types of electronic and ionic ingredients can exist stably in two completely different defect configurations*. The energy barrier for thermal conversion between the two different configurations must be high enough to prevent such a conversion over the whole temperature range of their thermal stability. This required high conversion-energy barrier makes model (A) highly unlikely due to its similarity to the unrelaxed excited U_2 center. For the mixed crowdion $[HCl^-]$ model (B), with its completely different ionic structure compared to the H_i^0

(U_2 center), a high conversion-energy barrier is much more likely.

D. OH⁻ photoreactions above 120 K

Above 100 K, one of the primary reaction-products of the OH⁻ photodissociation, the H_i^0 center, becomes thermally unstable. If an OH⁻-doped crystal, after low-temperature photodissociation into [O⁻] and H_i^0 centers, is thermally annealed into this temperature range, the U_2 band due to stabilized H_i^0 defects decays and the broad absorption around 540 nm characteristic for substitutional [H_2O^-] defects is formed.[22] Figure 17 shows the result of a direct photodissociation experiment in this temperature range. Monochromatic irradiation into the OH⁻ band leads to an effective bleaching of this band and a corresponding buildup of the H_2O^- absorption, with the two absorption changes showing a linear interrelation. After the primary photodissociation process

$$[OH^-] + h\nu \rightarrow [O^-] + H_i^0 \qquad (4)$$

the thermally mobile H_i^0 defect has, in principle, two possibilities for forming H_2O^- defects:
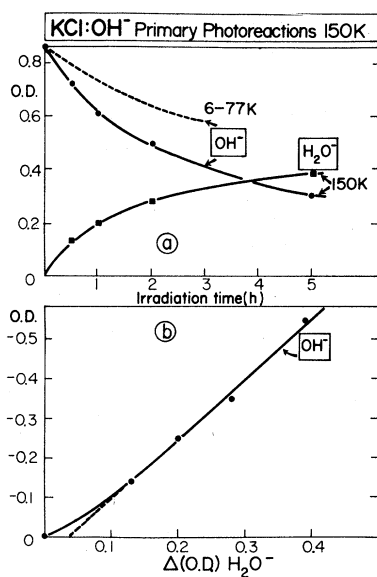
$$H_i^0 + [OH^-] \xrightarrow{kT} [H_2O^-] \qquad (6)$$

FIG. 17. Primary photoreaction of KCl:OH⁻ at 150 K. (a) Decrease of OH⁻ and increase of H_2O^- absorption as a function of irradiation time. (b) Linear correlation between observed decrease of OH⁻ and increase of H_2O^- band.

or

$$2H_i^0 + [O^-] \xrightarrow{kT} [H_2O^-]. \qquad (7)$$

At the very beginning of the photoconversion, only few [O⁻] defects are present. If reaction (7) would be the one responsible for the H_2O^- conversion, we would expect a very small H_2O^- formation rate at the beginning of the reaction, which should increase under longer irradiation. The opposite, however, is observed, namely, a high H_2O^- formation rate immediately at the beginning of the photoreaction (Fig. 17), which decreases under prolonged irradiation. This clearly selects reaction (6) as the operative process, so that together with the primary reaction [Eq. (4)] we have a net reaction

$$2[OH^-] + h\nu \rightarrow [O^-] + [H_2O^-]. \qquad (8)$$
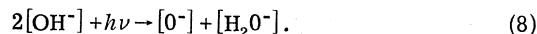
We see that two OH⁻ defects have to be destroyed in order to form one H_2O^- defect: One OH⁻ works after photoexcitation as the "donor" of a mobile H_i^0 [Eq. (4)], while another [OH⁻] defect works as the "acceptor" forming the [H_2O^-] center [Eq. (6)]. Comparing the initial decay rate of the OH⁻ band under light irradiation at 150 K to the rate observed in the temperature range up to 77 K (Fig. 17), we see that this rate has doubled in the high-temperature range. This reflects directly the fact that in contrast to the low-temperature range two OH⁻ defects are now consumed in photoreaction. This leads to the important result that the *primary photodissociation process of the OH⁻ itself* [*Eq.* (5)] *is completely temperature independent over the whole temperature range from* 6 K *up to at least* 150 K.

Above 250 K, the [H_2O^-] center decomposes so that in this range none of the treated primary and secondary reaction products (H_i^0, H_i^-, [Cl_2^-], [H_2O^-]) are thermally stable any more. In this high-temperature range (measured up to 300 K) one finds that the OH⁻ absorption becomes very stable against light irradiation. Even after hours of uv exposure, the OH⁻ band shows no notable decay, but only a very small "shift" to longer wavelength indicating that a small amount of U centers ([H⁻] defects) have been formed, together with small amounts of F centers. We believe that the low conversion efficiency is *not* caused by a temperature dependence of the primary photodissociation rate of Eq. (4). As this rate was found to be completely temperature independent up to 150 K, it is reasonable to assume that it remains this way in the high-temperature range

too. Under this assumption, the drastic reduction of the OH⁻ photodecomposition at high temperatures must be due to the fact that *no stable primary and secondary reaction products can be formed*, so that the back reaction into the original [OH⁻] defect is the most predominant secondary reaction. We can test this idea directly by supplying in the crystal some other point defects, which could act as a reaction partner and stabilizer for the thermally instable primary products

of the OH⁻ photodecomposition. We have done this in the form of F centers for the whole temperature range 6–300 K discussed here. The results of this work will be published elsewhere.[23]

---

*Present address: Instituto de Energia Atomica, São Paulo, Brazil.

[1] B. Fritz, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968).

[2] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. 104, 599 (1956).

[3] C. J. Delbecq, P. Pringsheim, and P. H. Yuster, J. Chem. Phys. 20, 746 (1952).

[4] B. Fritz, J. Phys. Chem. Solids 23, 375 (1962).

[5] W. Hayes and J. W. Hodby, Proc. R. Soc. London A294, 359 (1966).

[6] R. Hilsch and R. W. Pohl, Ann. Phys. (Leipzig) 32, 156 (1938).

[7] W. Martienssen, Z. Phys. 131, 488 (1952).

[8] M. de Souza and F. Lüty, Phys. Rev. B 8, 5866 (1973).

[9] W. Barth and B. Fritz, Phys. Status Solidi 19, 515 (1967).

[10] D. Pan and F. Lüty, Phys. Rev. B 18, 1968 (1978).

[11] F. Kerkhoff, Z. Phys. 158, 595 (1960).

[12] F. Kerkhoff, W. Martienssen, and W. Sander, Z. Phys.

173, 184 (1963).

[13] J. M. Spaeth and M. Storm, Phys. Status Solidi 42, 739 (1970).

[14] F. Fischer and H. Gründig, Z. Phys. 184, 299 (1965).

[15] F. Fischer, Z. Physik 187, 262 (1965).

[16] F. Fischer, Naturwissenschaften 54, 313 (1967).

[17] C. Z. van Doorn, Rev. Sci. Instrum. 32, 755 (1961).

[18] G. Kurz, Phys. Status Solidi 31, 93 (1969).

[19] W. Känzig and T. O. Woodruff, Phys. Chem. Solids 3, 509 (1958).

[20] C. J. Delbecq, E. Hutchinson, D. Schoemaker, E. C. Yasaitis, and P. H. Yuster, Phys. Rev. 187, 1103 (1969); F. W. Patten and F. J. Keller, *ibid.* 187, 1120 (1969).

[21] E. Sander and W. A. Sibley, in *Point Defects in Solids*, edited by J. H. Crawford and C. M. Slifkin (Plenum, New York, 1972), Vol. 1.

[22] W. Rusch and H. Seidel, Solid State Commun. 9, 231 (1971).

[23] S. P. Morato and F. Lüty (unpublished).