HYDROGEN TRANSPORT PROCESS IN OH⁻ DOPED KCl AND KBr*

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It was investigated the kinectics of formation and destruction of hydrogen related defects originated from the randon aggregation of hydrogen atoms in their ground state that were allowed to diffuse through the crystal after the photodissociation of OH⁻ defects. Formation and activation energies for the several processes involved in three main steps were obtained utilizing 1st. order kinectics. A model for a new U_{2x} center is proposed.

In a preliminary study on the kinectics of U_2 to H_2O defects conversion after the photo dissociation of OH⁻ ions in alkali halides it was shown[1] that the resulting hydrogen atom diffuses in the dark with a thermally assisted motion that brings this atom into two different configurations. In one configuration the hydrogen atom remains trapped by an OH⁻ ion forming a sort of H_i^o - OH⁻ association (U_{2x} center) that produces electronic absorptions in the UV (45000 cm⁻¹ for KCl and 40000 cm⁻¹ for KBr). The other configuration is the H_2O^- defect itself that is produced by a direct and definitive trapping of the H_i^o atom by one OH⁻ ion forming with it a water molecule in a substitutional position and imbebed in an electronic cloud also with independent electronic absorption[2,3]. These two configurations are produced via reaction channels that compete with each other at the expenses of available and mobile hydrogen atoms and substitutional static OH⁻ impurities. In the sequence of creation and anihilation processes that originated from the photodissociation of the OH⁻ ion, before the nearly complete restoration of the original OH⁻ concentration, F and U centers are also formed. In this work we investigate the mechanisms behing these atomic and ionic transport processes that take place with the participating centers in their ground state.

The experimental procedures followed standard techniques of optical absorption at low temperatures. Typical 10x5x1 mm³ samples were cleaved from boules of KCl and KBr doped with KOH at 10⁻⁴ mole % grown in our laboratory by a Czochralski method from U.P. grade material. Optical absorption measurements were performed with a Cary 17D spectrophotometer utilizing an optical cryostat from Janis, model 8DT provided with a gas exchange chamber as a thermal switch. Temperature was controlled and measured with copper-constantan thermocouples referred to an electronic ice point reference. The photodissociation of OH⁻ was done with a resonant wavelenght provided by a xenon lamp plus a monochromator. The samples were pulse annealed under a programmed routine to allow a reproducible dT/dt shape and then cooled to LNT for the optical measurement.

The thermally assisted formation and destruction processes were analysed utilizing first order kinetics where applicable, following the procedure done by Fritz[4] and under the assumption that after the initial dissociation of the OH⁻ ion, only one mobile entity[5] is responsible for the formation of one or more independent defects, after being trapped at different sites. In figures 1 and 2 there are shown for KCl and KBr respectively the behaviour of the absorption bands maxima of the defects involved plotted against the annealing temperature and after the initial dissociation of the OH⁻. In these sequences of destruction/ creation of defects that start with the destruction of the U_2 center, several intermediate defects appear and disappear. In both cases these sequences end up with F and U centers. After prolonged stay of the sample in the dark at room temperature, these two centers also disappear and restore the OH⁻ concentration to almost its initial value.

The full cycle of defects transformation was divided into three main steps, each of them characterized by the thermal extinction of one defect. These steps occured when the extinction of U_2, U_{2x} and H_2O^- took place. The temperatures of maximum chance (dn/dT = max) indicated in table 1 correlate precisely the extinction of one defect with the appearance of one or more defects, at the expenses of the destroyed one. In this table there are shown activation energies obtained by fitting the three regions of interest from curves of figures 1 and 2 with a first order kinetics. Below the activation energy values it is shown the percent population of centers destroyed or created. These percentual values represent the probabilities that a certain reaction channel occurs, taking into consideration the concentration and oscillator strengths of the centers
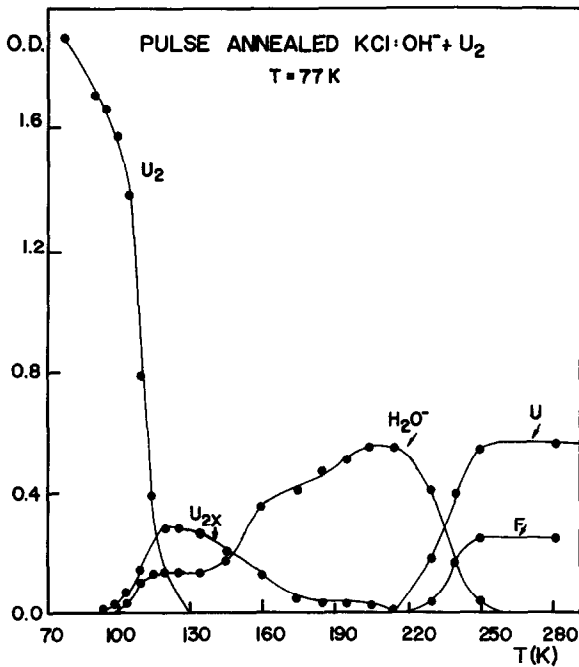
Figure 1 - Absorption bands maxima at 77 K for pul
se annealed KCL:OH⁻+ U₂ system   after
the photodissociation of OH⁻. In   the
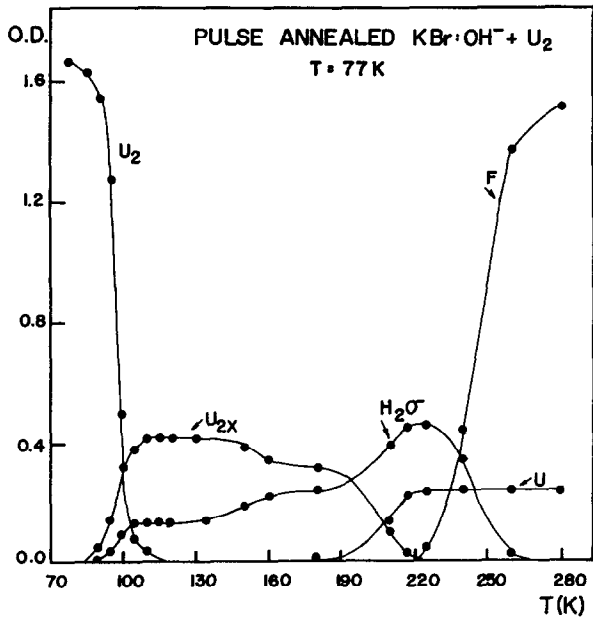final step U centers are preferentially
formed.

Figure 2 - Absorption bands maxima at 77 K for pul
se annealed KBr:OH⁻ + U₂ system   after
the photodissociation of OH⁻. In this
case F centers are preferentially for
med in the final step.

involved as done previously[1]. It is important
to note that these probability values are ob
tained independently from the activation energies
that resulted from the fitting of the kinectic
curves.

In the first step the extinction of the U_2
center leads to the formation of U_{2x} and H_2O^-
centers. The temperature dependence of the U_2
concentration yielded activation energies   of
0.10 eV for KCl and 0.13 eV for KBr. This pure
ly atomic process involving thermal migration
and trapping of the hydrogen atom, takes place
in the dark and consequently with this atom in
its ground state. In this way a U_2 center
which is forced to move from its stable inters
titial position by a phonon mechanism, produces
U_2 related defects without lattice Jahn-Teller
distortion or crowdion creation that are ob
served by the photo-excitation of the U_2 center
at low temperatures[6]. Consequently   distinct
defects are produced that do not change the bas
ic lattice defect configuration since no pola
rization effects due to optical   excitation
change the lowest empty 4s type orbital (K^+) of
the conduction band. These low activation ener
gy values for the hydrogen atom to escape
(while in its ground electronic state) reflect
its small size and charge neutrality and, conse
quently, a shallow potential well where it was
trapped. In spite of diffusing in its ground
state the hydrogen atom has low energy values
that resemble photon assisted process of ionic
diffusion of point defects in their excited sta
te, what is well known for lowering the step dif
fusion activation energies of centers such as
the F_A[7].

The formation energies necessary to pro
duce U_{2x} and H_2O^- centers indicate in KBr
that since U_{2x} centers have a lower forma
tion energy than H_2O^- centers (0.15 vs 0.19 eV)
U_{2x} centers are preferentially formed and
in larger number (for KCl the U_{2x} is not a
resolved band so no correlation was possible).
This was consistently observed through the num
ber of centers produced after the 100% destruc
tion of U_2 that produces 34% of U_{2x} and 16% of
H_2O^- centers. The remaining 50% of U_2 centers
not accounted for are possibly aggregated into
H_2 molecules that are invisible by optical
techniques. In this step, the rates of formation
involved are dependent on the available OH⁻
defects left without being photodissociated to
provide the necessary number of traps for U_2
centers to aggregate. In this work the initial
OH⁻ photodissociation was limited to 35% of the
original OH⁻ concentration. It should be pointed
out that a certain number of U_2 centers react
back with O⁻ defects producing OH⁻ centers. This
back process was verified through a thermally
assisted luminescence[8] that is produced by the
de-excitation of OH⁻ defects formed in their
excited state after the capture of the hydrogen
atom by the substitutional O⁻ defect left by
the initial OH⁻ photodissociation. By this way
the number of available OH⁻ traps is in fact
larger than the quantity left after the OH⁻ pho
todissociation. To the statistically available
OH⁻ traps one should consider the dynamically
produced ones that will increase the total number

Table 1. Destruction and formation energies of the different centers involved in this study, for KCl and KBr in the three main temperature steps. The temperature where dn/dt is maximum is indicated in parenthesis for each crystal. The numbers in percent correspond to the amount of centers involved in each step. Energies are in eV.

Step	Crystal (T)	Destruction Energy			Formation Energy			
		U_2	U_{2x}	H_2O^-	U_{2x}	H_2O^-	F	U
I	KCl (100K)	0.10 100%			0.19 ?	0.19 ?		
	KBr (95K)	0.13 100%			0.15 34%	0.19 16%		
II	KCl (140K)		0.18 100%		0.19 100%			
	KBr (205K)		0.36 100%		0.34 55%			0.37 45%
III	KCl (230K)			0.55 100%		0.80 14%		0.51 57%
	KBr (245K)			0.46 100%		0.46 100%		

of traps for the hydrogen atom to interact with. What happens next to a U_{2x} centers is its final transformation into a H_2O^x center. For KCl this conversion is complete what is justified in part by a lower temperature of stabilization and a smaller activation energy when compared to KBr where the production of U centers also results as a competitive reaction channel. In the second and third steps a general trend verified before is again observed: energy values are balanced by the respective densities of the centers involved. Long range hydrogen atom transport is no longer observed as more stable complex hydrogen aggregates appear.

The results obtained with the U_2 center migration and aggregation into U_{2x} and H_2O^- centers added by the step transformation of U_{2x} into H_2O^- and, finally, the destruction of the H_2O^- center itself indicate that the highest "thermal"

energy barrier that the hydrogen atom in its ground state has to overcome to form an H_2O^- defect must confine this atom in one of the 24 available interstitital sites next nearest neighbours to the OH$^-$ defect. The hydrogen atom thus trapped in one of these sites "feels" the polarization effect due to the OH$^-$ and forms the U_{2x} center but only with one transition of higher energy than the unperturbed U_2 center and without splitting this transition as it happens with strongly perturbed U_2 center[9]. This polarization effect weakly affects the U_2 center resulting in the U_{2x} transition and confines the hydrogen atom into a more thermally stable place. We are presently extending this study to other alkali halide lattices and working with ESR techniques to confirm the present proposal of the U_{2x} center configurational model.

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