

## $\text{H}_2\text{O}^-$ DEFECTS IN ALKALI HALIDES†

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The production of  $\text{H}_2\text{O}^-$  defects in alkali halides doped with  $\text{OH}^-$  impurities was studied at different temperatures. It was found that  $\text{H}_2\text{O}^-$  defects can be formed either directly by the thermal annealing of  $\text{U}_2$  centers that get captured by  $\text{OH}^-$  defects or indirectly after the extinction of the  $\text{U}_{2x}$  center, an intermediate specimen composed by an  $\text{U}_2$  center pre-captured by an  $\text{OH}^-$  defect. Several new properties of the  $\text{H}_2\text{O}^-$  defect were found and studied. These centers are photodissociated at low temperatures with an efficiency that decreases with increasing temperature and at the expenses of very low activation energies (0.01 eV). The total  $\text{H}_2\text{O}^-$  absorption oscillator strength was found to be 0.62 and its integrated absorption did not vary with temperature in this thermal stability range. The structure of the  $\text{H}_2\text{O}^-$  band was decomposed and best fit by a sum of 5 gaussians. The integrated absorption of the individual component bands changed with temperature indicating a redistribution of electronic transitions with a possible modification of the configurational symmetry of the  $\text{H}_2\text{O}^-$  center at high temperatures but with conservation of the total electronic charge. Close to its thermal dissociation limit the  $\text{H}_2\text{O}^-$  center smoothly changes into an F center that independently traps an OH molecule and a H atom.

### INTRODUCTION

The resonant photodissociation of  $\text{OH}^-$  impurities in alkali halides at low temperatures is a well-known process that directly produces hydrogen and oxygen centers. These centers are primarily interstitial hydrogen atoms ( $\text{U}_2$  centers) and substitutional oxygen ions.<sup>1,2</sup> Optical and/or thermal stimulation of a crystal containing such centers can lead to a complex chain of defects such as  $\text{H}_x$ ,  $\text{U}_{2x}$  and  $\text{H}_2\text{O}^-$  centers.<sup>3,4</sup>  $\text{H}_2\text{O}^-$  centers were first discovered by Rush and Seidel<sup>5,6</sup> who did only low temperature studies. Further studies at higher temperatures showed that this center can be produced either directly from the photodissociation of the  $\text{OH}^-$  center or via a two-step thermally assisted mechanism that initially produces  $\text{U}_{2x}$  and  $\text{H}_2\text{O}^-$  centers from the thermal dissociation of the  $\text{U}_2$  center and secondly from the direct conversion of the  $\text{U}_{2x}$  into the  $\text{H}_2\text{O}^-$  center.<sup>4</sup>

The kinetics of these transport processes which aggregate hydrogen and oxygen centers in their ground states has been recently reported.<sup>7</sup> In the present work we report the results of an investigation on the  $\text{H}_2\text{O}^-$  optical properties at high temperatures that corroborate the configurational model of the  $\text{U}_{2x}$  center earlier proposed as being  $\text{U}_2$  center pre-captured by an  $\text{OH}^-$  center. The importance of such a study remains in the fact that the understanding of hydrogen and oxygen defects properties is very useful in the development of color center lasers, since being in general negatively charged, these defects favor the formation of ionized F center aggregates like the  $\text{F}_2^+$  stabilized by efficient electron traps.<sup>8,9</sup>

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## EXPERIMENTAL

The experimental methodology followed a standard low temperature procedure utilizing an optical cryostat for absorption measurements. Low temperature at the sample was obtained with a Janis 8DT cryostat provided with windows allowing perpendicular optical paths and a gas exchange chamber as a thermal switch. Optical absorption measurements were made with a Zeiss DMR 21 and a PE 180 spectrophotometers. Temperature was controlled and measured with copper constantan thermocouples using an ice point as the zero degree reference. Typical  $10 \times 5 \times 1 \text{ mm}^3$  alkali halide samples were cleaved from boules of crystals doped with  $\text{OH}^-$  at approximately  $10^{-4}$  mole%. The crystals were grown in our laboratory by the Czochralski technique from U.P. grade material.

## RESULTS AND DISCUSSION

The  $\text{H}_2\text{O}^-$  center is a general defect. It can be produced in any alkali halide crystal following the  $\text{OH}^-$  photodissociation,  $\text{U}_2$  and  $\text{U}_{2x}$  centers thermal annealing. Figure 1

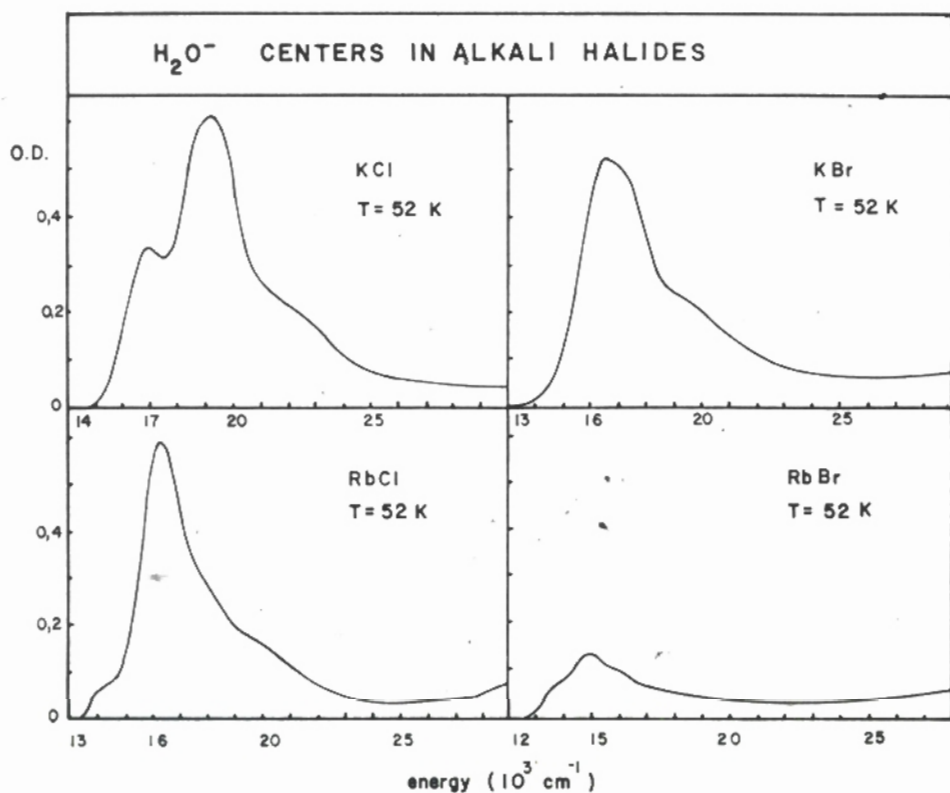
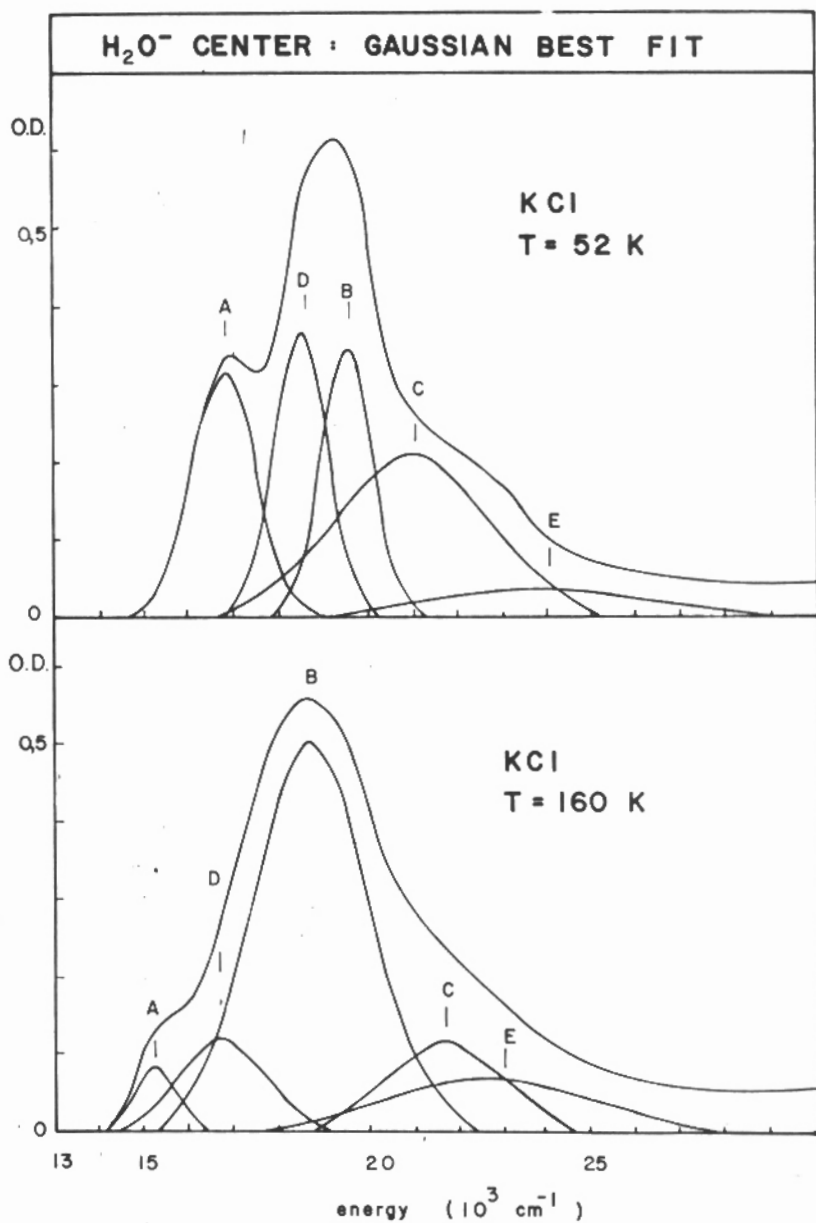


FIGURE 1  $\text{H}_2\text{O}^-$  centers in four alkali halides.

FIGURE 2 Computer decomposition of the  $\text{H}_2\text{O}^-$  band into 5 gaussians at 52 and 160 K.

shows the  $\text{H}_2\text{O}^-$  center in four alkali halides. A Molwo-Ivey relationship was obtained for these crystals at 77 K taking the wavelength at maximum optical densities. A least square fit produced:

$$\lambda_{\max} = 163.64 a^{3.04}$$

A weak infrared single absorption band was observed at  $1410 \text{ cm}^{-1}$  for KCl at 77 K that could be assigned to a transition of the  $\text{H}_2\text{O}^-$  center since a direct correlation of this transition with the visible absorption of the center could be obtained. An almost "pure" isotope shift effect in this transition was also observed for KCl:OD<sup>-</sup> with:

$$\frac{\omega(\text{H}_2\text{O}^-)}{\omega(\text{D}_2\text{O}^-)} = 1.343$$

a value which differs by 5% of  $\sqrt{2}$  thus indicating the presence of an isolated weakly charged hydrogen.

The main visible optical absorption band of the  $\text{H}_2\text{O}^-$  center shows a structure that can be decomposed into at least four Gaussian components. A computer program based on the sum of Gaussians was developed to adjust the spectra of the  $\text{H}_2\text{O}^-$  absorption bands. The smaller deviations from experimental values were obtained with a best fit of a sum of 5 gaussians. In Figure 2 it is shown the decomposition of the absorption band into its components at 52 and at 160 K in KCl. The adjusted parameters are shown in Table I. It should be pointed out that whereas the integrated absorption remains practically constant within 3%, by varying the temperature from 52 to 160 K, the individual components show dramatic, even though, reversible changes. These results suggest the occurrence of distortions of the defect with temperature that could cause rearrangements of the transition probabilities.

TABLE I

Gaussian bands parameters of the 5 components of the  $\text{H}_2\text{O}^-$  center at 52 and at 160 K in KCl

	$\lambda_{\max}$ ( $\text{cm}^{-1}$ )		H ( $\text{cm}^{-1}$ )		Peak height (O.D.)		Band area Total area $\times 100\%$	
	52 K	160 K	52 K	160 K	52 K	160 K	52 K	160 K
A	16,838	15,220	694	472	0.316	0.084	20.4%	3.6%
D	18,572	16,759	594	958	0.366	0.117	20.2%	10.1%
B	19,604	18,691	579	1276	0.348	0.502	18.7%	58.2%
C	21,045	21,636	1728	1318	0.206	0.114	33%	13.7%
E	23,860	22,641	2351	2304	0.035	0.069	7.7%	14.4%

It was found that  $\text{H}_2\text{O}^-$  centers undergo photodissociation at low temperatures. This was observed in the same four samples mentioned before. Two main experiments were performed with KCl, the first one basically to demonstrate that the main products of the  $\text{H}_2\text{O}^-$  dissociation are  $\text{U}_2$  and  $\text{OH}^-$  centers (experiment A). This is shown in Figure 3 by a direct correlation of the  $\text{H}_2\text{O}^-$  center destruction with the  $\text{U}_2$

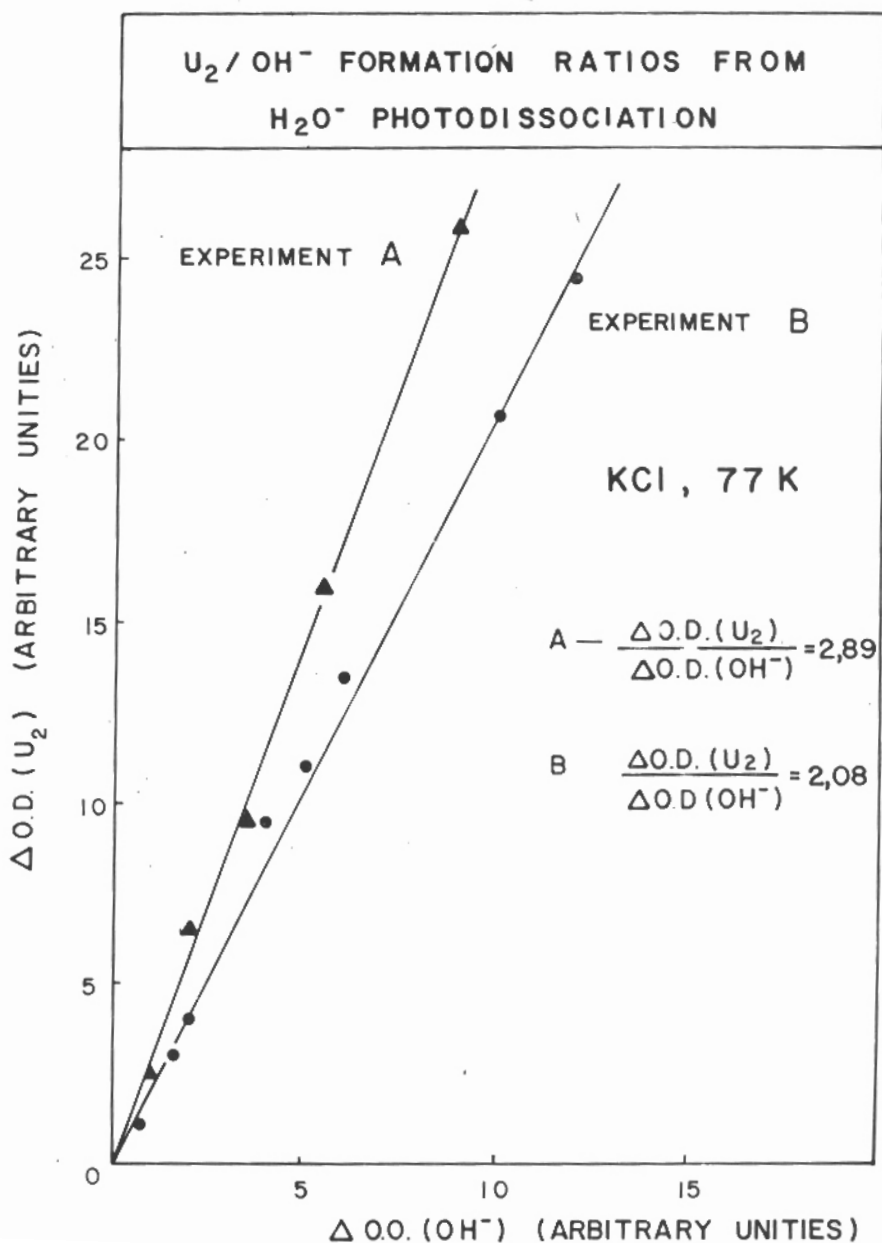
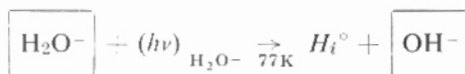


FIGURE 3 Correlation of the H<sub>2</sub>O<sup>-</sup> photodissociation at 77 K with the creation of U<sub>2</sub> and OH<sup>-</sup> centers. In experiment A this dissociation was done in the presence of a lower concentration of O<sup>-</sup> centers than in experiment B.

and OH<sup>-</sup> center formation. In this sample the original OH<sup>-</sup> concentration was previously decreased by 33% in the OH<sup>-</sup> dissociation process. The overall result of this experiment can be summarized by:



From Figure 3 taking the ratios between the optical densities of U<sub>2</sub> and OH<sup>-</sup>, and using the Smakula relation, one obtains a factor of 0.90 for the ratio of changes in concentration of these two centers. This means that the concentration of OH<sup>-</sup> produced in this process is at least 10% greater than the concentration of U<sub>2</sub> centers since no other defects were observed optically. In this case U<sub>2</sub> centers might have combined with available O<sup>-</sup> centers directly producing OH<sup>-</sup> centers—during the whole process O<sup>-</sup> centers were always present. To verify this proposition another experiment was made with a sample where 42% of the original OH<sup>-</sup> centers were initially converted into O<sup>-</sup> and U<sub>2</sub> centers (experiment B). In this case, in the presence of a larger OH<sup>-</sup> concentration, the dissociation of H<sub>2</sub>O<sup>-</sup> centers produced a different ratio of U<sub>2</sub> to OH<sup>-</sup> centers. Now the relative concentration of OH<sup>-</sup> centers is 35% greater than the U<sub>2</sub> center concentration. This confirms the previous hypothesis that the excess of OH<sup>-</sup> centers produced by the H<sub>2</sub>O<sup>-</sup> dissociation is a function of the O<sup>-</sup> concentration in the sample.

Considering that H<sub>2</sub>O<sup>-</sup> centers are decomposed into U<sub>2</sub> and OH<sup>-</sup> centers in a 1-to-1 ratio, taking the integrated absorptions and the known oscillator strengths of the centers involved and applying again the Smakula relation, it was obtained  $f = 0.62$  as the total oscillator strength of the H<sub>2</sub>O<sup>-</sup> center. Since the integrated absorption does not vary with temperature (within 52 to 160 K) and assuming a constant total  $f$  number the individual  $f$  values for the 5 bands were obtained and are listed in Table II.

TABLE II  
 $f$  numbers of the gaussian components of the  
H<sub>2</sub>O<sup>-</sup> center in KCl

	Oscillator strength	
	$T=52\text{ K}$	$T=160\text{ K}$
A	0.13	0.02
D	0.13	0.06
B	0.12	0.36
C	0.21	0.08
E	0.05	0.09

In some cases the  $f$  variation is by a factor of 5 (A band) what indicates a drastic change in the configuration of the center. At low temperatures, the water molecule transitions band A (transition moment parallel to the  $\langle 111 \rangle$  dipole axis) and band B (transition moment perpendicular to the  $\langle 111 \rangle$  dipole axis) are clearly seen. The

change of symmetry with temperature distorts this molecule centering the electronic charge into one transition (B transition) that clearly approaches the F center configuration with the electron more evenly distributed within the vacancy.

The temperature dependence of the photodissociation process was studied from 52 to 150 K always illuminating on the band maximum. The optical density decreased exponentially according to:

$$\text{O.D.} = (\text{O.D.})_0 \exp(t/\tau)$$

where

$$\tau = \tau_0 \exp(-E/KT)$$

$\tau$  being the half-life and  $E$  the thermal activation energy.

Two opposite effects were found in the 42 to 150 K range. Above 120 K a  $\ln \tau \propto T^{-1}$  law was found meaning a typical thermally activated photodissociation process Arrhenius type dependence with a very low activation energy (0.01 eV). This indicated a weak bond among center components when in the excited state. Below 120 K a  $\ln \tau \propto T$  law was found that was interpreted as due to the change with  $T$  of the relative intensities of the component bands. Since illumination was always at maximum O.D., it was acting differently in these two  $T$  regions. This effect also corroborated the idea that the morphology of the H<sub>2</sub>O<sup>-</sup> center drastically changed with  $T$ , above 52 K.

The thermal destruction of the H<sub>2</sub>O<sup>-</sup> center was obtained by annealing the crystal to room temperature. As mentioned in a previous work this process produced U and F centers.

## CONCLUSIONS

The above results led us to conclude that the H<sub>2</sub>O<sup>-</sup> center model originally proposed as a water molecule embedded in an F center, is valid only at low temperatures. From the observed effects:

- a) The process of thermal creation involving U<sub>2</sub> with OH<sup>-</sup> or U<sub>2x</sub> centers,
- b) The optical dissociation producing U<sub>2</sub> and OH<sup>-</sup> centers with a very low activation energy.
- c) The thermal extinction producing F and U centers.
- d) The indication via an IR transition of an isolated proton and its isotope effect.
- e) The change in  $f$  number of the component bands with the conservation of the electronic charge of the center.

It is proposed tentatively that one proton of the water molecule becomes repelled from the OH<sup>0</sup> at higher temperatures (reversible process) forming a type of H-OH configuration embedded in the F center thus losing the water molecule characteristic. The main transition (B band) smoothly approaches the 1s to the 2p triply degenerated state of the F center.

This model/mechanism which is supported by optical data alone opens a very interesting line for investigation with other techniques that could bring additional quantitative proof for this proposition.

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