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PHOTOCHEMISTRY AND REACTIONS OF OH^- DEFECTS AND *F* CENTERS IN ALKALI HALIDES†

SPERO PENHA MORATO‡ and FRITZ LÜTY
Physics Department, University of Utah, Salt Lake City, UT 84112, U.S.A.

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Abstract—Additively colored $KCl:OH^-$ crystals show under combined UV and visible irradiation an irreversible destruction of *F* centers and visible absorption. This process, which is effective over the whole temperature range 4–300 K, was studied systematically in terms of the reaction efficiency and products using UV-visible and IR (local mode) spectroscopy. The UV photo-dissociation of OH^- defects and photo-ionization of *F* centers produce a combined net effect, in which at higher temperatures all *F* centers are converted into *U* centers, thus completely bleaching the colored crystal. By these photo-reactions, high contrast visible images can be produced which are stable under visible light at *RT*, and are thermally stable up to 650°C. Besides the optical information-storage aspect, these photo-reactions can be used for controlled production of U_A centers if the crystal contains alkali-ion impurities like Na^+.

1. INTRODUCTION

Substitutional OH^- ions in alkali-halides, when irradiated with UV light in their electronic absorption band (at 204 nm in KCl), become photodissociated[1, 2]. This process, which is operative with high efficiency over the whole temperature range from 4 to 300 K, leads to a variety of primary and secondary reaction products, which have been systematically studied and reviewed in a parallel work[3]. For further characterization and testing of these reaction products and their mobility and reactivity, we introduce in this work *F* centers as point-defect probes additionally to the OH^- defects. This is achieved by additive coloration of the $KCl:OH^-$ crystal. If the OH^- content is not too high—we used $N(OH^-) < 10^{-4}$—additive coloration works like in pure crystals and does not lead to any noticeable change or conversion of the OH^- defects (as tested by their optical absorption properties). This mixed system of stable *F* centers and OH^- defects was studied over the whole temperature range 4–300 K for the photo-chemical conversions and reaction products under controlled UV and/or visible light irradiation, in comparison to parallel experiments in uncolored $KCl:OH^-$ crystals. As will be seen, the presence of the *F* centers (with or without photo excitation) affects the photochemistry of the OH^- dissociation in a profound way, leading to stable bleaching effects of the colored crystal in the visible range. Besides interesting aspects for optical information storage, the interaction and interrelation of OH^- and *F* center systems in general have recently come in the focus of interest due to the role of OH^- defects and their reaction products for the stabilization of *F*-aggregate centers in connection with their application as tuneable IR laser material[4]. We will show further, that a controlled use of the photo-reactions of the mixed defect system can be used to convert *F*-aggregates (like the $F_A(Na^+)$ center) into the corresponding *U*-aggregate (e.g. U_A) centers.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Photo-excitation of OH^- defects by UV light irradiation into the electronic OH^- absorption band leads to a primary dissociation process which is operative *over the whole range from* He *to room-temperature*, according to the following reaction

$$\boxed{OH^-} + h\nu \rightarrow \boxed{O^-} + H_i^0. \qquad (1)$$

Photo-excitation of *F* centers, on the other hand, depends in its results on temperature and photon energy. Low energy photon (< 2.5 eV) excitation, populates at low temperatures ($T < 90$ K) only the relaxed excited *F* state[5], but leads at higher temperature to photo-ionization of the electron. High energy photon excitation into the conductive states of the *L* bands[6] produces at *all* temperatures photo-ionization

$$\boxed{e^-} + h\nu \rightarrow \boxed{-} + e^-. \qquad (2)$$

Depending on the thermal stability of the reaction products of eqns (1) and (2), we obtain very different results in the combined photo-chemistry of the two defects. We therefore divide the presentation of the results into different temperature ranges, which are relevant for the stability of reaction products.

(1) *Low temperature processes*

Below 120 K, the ejected hydrogen atom from reaction eqn (1) is stabilized as an interstitial hydrogen atom H_i^0(U_2 center). The primary photo-dissociation of the OH^- therefore leads to a decrease of the OH^- band and a corresponding increase of the U_2 band and the O^- absorption[2, 3]. In an additively colored KCl crystal the same type of optical conversions is observed in the UV range after UV irradiation (Fig. 1). Additionally,

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

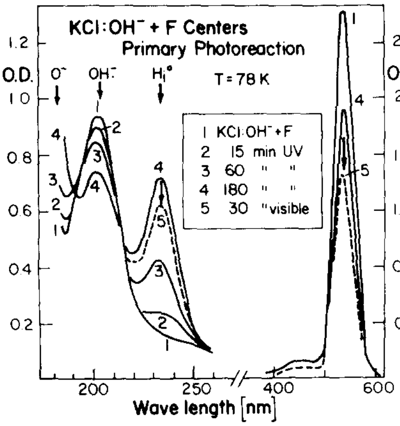

Fig. 1. UV and visible absorption spectra of an additively colored KCl:OH⁻ crystal, before and after monochromatic UV irradiation (204 nm) and subsequent visible light irradiation.

however, the *F band is found to decrease* during these processes. Figure 2 shows these spectral changes as a function of UV irradiation time in comparison to a KCl:OH⁻ crystal without *F* centers. We find that the—temperature independent—primary OH⁻ destruction rate is *not affected* by the presence of the *F* centers. The formation rate of U_2 centers, however, has been reduced by the presence of the *F* centers, and the *F* centers themselves show a decay during these reactions (all effects are temperature independent). A plot of the OH⁻ band decrease vs the U_2 band increase (Fig. 3) shows for both types of crystals a straight line dependence, but with a different slope, indicating a lower $U_2(=H_i^0)$ formation for the colored crystal.

A careful analysis of the number of H_i^0 and *F* centers involved in this process shows that the amount of *F* centers reduced during the OH⁻ photodissociation process corresponds quantitatively to the difference between the H_i^0 centers produced in the two crystals, namely KCl:OH⁻ and KCl:OH⁻ + *F*. This indicates that in both cases the same $OH^- \rightarrow H_i^0$ conversion takes place, but that in the presence of *F* centers a *part of the created* H_i^0 *centers react with a part of the available* F *centers.*

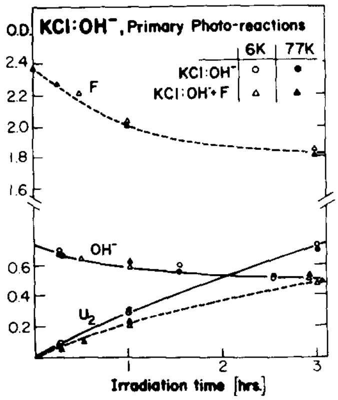

Fig. 2. Increase and decay of the OH⁻, U_2 and *F* band absorption as a function of (204 nm) UV irradiation time at 6 and 77 K in an uncolored and additively colored KCl:OH⁻ crystal.

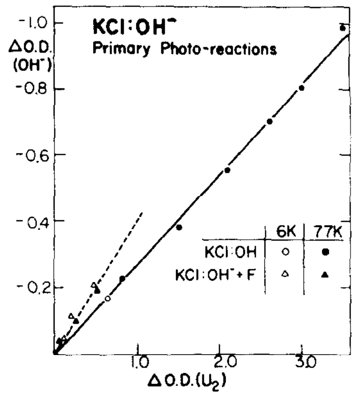

Fig. 3. Decrease of the OH⁻ band absorption vs increase of the U_2 band absorption under UV light irradiation at 6 and 77 K for an uncolored and additively colored KCl:OH⁻ crystal.

After the observation of these effects an immediate question arises: What is formed out of the H_i^0 and *F* centers which are consumed in this process? Two evident answers may be anticipated: either the created interstitial hydrogen atom, while moving away from the dissociated OH⁻ site, gets captured by a nearby *F* center, thus creating the H⁻ center (*U* band); or an *F* center ionization takes place in the process and the freed electron will meet a stabilized H_i^0 center and forms the H_i^- center (U_1 band). The first possibility is clearly excluded, because no trace of the (high oscillator strength) *U* band is observed in this process. The weak and very broad U_1 band due to H_i^- interstitials is much harder to detect. We could however confirm the presence of the second process by illuminating (after UV photodissociation) with visible light into the *F* band (see Fig. 1). In doing so, we obtained a further concentration reduction of both *F* and H_i^0 centers (Fig. 1). We therefore assume that already during the UV irradiation some *F* centers will be ionized by irradiation into their conductive states (*L* bands).

In addition to the reactions (eqns 1 and 2) we thus expect in this primary range the secondary reaction

$$e^- + H_i^0 \rightarrow H_i^-. \qquad (3)$$

(2) *Thermal annealing above* 120 K *and photochemical processes at* 150 K

Figure 4 shows in stages 1 and 2 the same absorption changes in the OH⁻, U_2 and *F* band as in Fig. 1, obtained by LNT UV irradiation. In order to test the postulated presence of H_i^- defects, we set up parallel experiments with IR spectroscopy. As shown on the right side of Fig. 4, we observe indeed at this stage (2) the presence of the H_i^- local mode[7] and a total absence of a H⁻ local mode. This confirms our interpretation of the low-temperature photo-chemistry in terms of eqns (1)–(3), which added together yield the net reaction:

$$\boxed{OH^-} + \boxed{e^-} + h\nu \rightarrow \boxed{O^-} + \boxed{-} + H_i^-. \qquad (4)$$

If we pulse-anneal this photo-decomposed system to

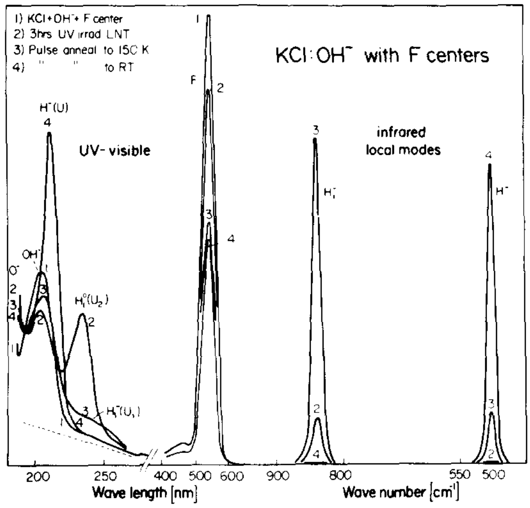

Fig. 4. UV-visible and IR local mode spectra of an additively colored KCl:OH⁻ crystal before and after the indicated UV irradiation and pulse annealing processes.

150 K (Step 3 in Fig. 4) we observe a strong increase of the H_i^- local mode band and a decrease in the F band (besides the thermal destruction of the U_2 band). The thermal annealing process makes the H_i^0 mobile. When it gets conveniently close to the F center, a transfer of the electron to the H_i^0 defect will take place, forming the H_i^- defect:

$$\boxed{e^-} + H_i^0 + kT \rightarrow H_i^- + \boxed{-} \tag{5}$$

As no light irradiation and photo-excitation is involved in this process, we must assume that the *F center electron in its ground state has the ability to tunnel into a nearby* H_i^0 *defect.* It is interesting to ask, over what distance this electron transfer by tunneling is working. The fact that the H_i^- defects formed by reaction (5) are stable at 150 K excludes a very small distance, because $H_i^-/\boxed{-}$ pairs would no longer be stable at 150 K. Moreover, they would exhibit a H_i^- local mode split by the interaction effect of the H_i^0 ion with the close-by vacancy[7], which we don't observe. The minimum separation from the vacancy for a thermally stable uncorrelated H^- interstitial with unsplit local mode was estimated in Ref. [7] to be about five times the interionic distance, so that the tunneling effect in eqn (5) apparently works over this distance. The relatively small amount of local mode absorption from substitutional H^-, formed in this thermal annealing stage (Fig. 4, step 3) indicates that only a small fraction of the electron tunneling occurs at distances, for which the $H_i^-/\boxed{-}$ pair is no longer stable and recombines into the $\boxed{H^-}$ configuration. Therefore, we conclude that the reaction of thermally mobile H_i^0 defects with F centers (in the ground state) leads always first to the electron transfer reaction (eqn 5), and *not to a direct process*

$$\boxed{e^-} + H_i^0 + kT \rightarrow \boxed{H^-}. \tag{6}$$

Under further thermal annealing to temperatures above 200 K (step 4 in Fig. 4), the uncorrelated H_i^- defects become mobile and eventually will be trapped by their anti-centers—the anion vacancy—forming the $\boxed{H^-}$ centers. This process, can clearly be observed in Fig. 4, showing the effect of the reaction:

$$H_i + \boxed{-} + kT \rightarrow \boxed{H^-}. \tag{7}$$

After this last process was completed we observe that the total amount of F center reduction corresponds to the total amount of U centers created. This fact confirms the above proposed equations to describe our observations. Adding all the equations that describe the OH^- initial photodecomposition (eqns 1–3) and the thermal processes up to RT (eqns 6, 7) we end up with the net reaction:

$$\boxed{OH^-} + \boxed{e^-} + h\nu + kT \rightarrow \boxed{O^-} + \boxed{H^-}. \tag{8}$$

If the photochemical reaction is directly performed in the temperature range of H_i^0 thermal instability, we observe under UV irradiation (150 K) a direct efficient destruction of F centers and formation of $\boxed{H^-}$ and H_i^- defects (Fig. 5). The addition of F light to the UV irradiation does not influence the F center decay process, as seen in the insert of Fig. 5. This leads us to conclude again that the electron transfer from an F center to a passing-by mobile H_i^0 defect (eqn 6) is efficiently operative without the need for an optically induced excitation or ionization process of the F electron. We should note that in this temperature range the presence of the F centers has completely changed the OH^- photochemistry. In the pure KCl:OH⁻ crystal without F centers, the OH^- photo-decomposition leads to full conversion into $\boxed{H_2O^-}$ defects[3], while in the crystal with F centers $\boxed{H^-}$ and H_i^- defects are the predominant stable reaction products.

(3) *Room temperature processes*

Above 250 K a new parameter enters into the photoreactions: Optical excitation of the F center leads not

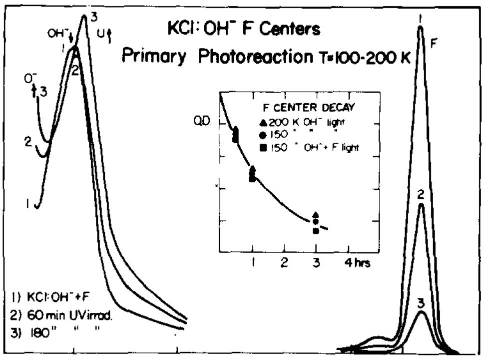

Fig. 5. Spectral changes obtained in an additively colored KCl:OH⁻ crystal by UV (204 nm) irradiation at 150 and 200 K.

only to ionization of the electron (eqn 2), but to ionic mobility of the anion vacancy, producing the well-known aggregation of *F* centers into *F*-aggregate ($F_2, F_3, \ldots$) defects[5]. In order to avoid this process, we used for the UV light irradiation two monochromators in tandem with a deuterium instead of a xenon light source. After the required very long exposure time, we observe the result shown in Fig. 6(b): The *F* band has decreased—without any indication of *F* center aggregation—and the UV spectral changes show the formation of *U* centers, everything very similar to the result at 150 K in Fig. 5. Clearly the primary OH^- photo-decomposition process is still operative leading together with the *F* centers to stable $\boxed{H^-}$ defects according to eqn (8). This is an important result, because in a pure KCl:OH^- crystal without *F* centers (Fig. 6a) even a very much higher UV exposure leads only to negligible small OH^- photo-decomposition[3]. This apparent "stability" of the OH^- defect against photo-decomposition can *not* be caused by a low primary photo-decomposition rate (eqn 1) at high temperatures, but must be due to the *thermal instability of the primary and secondary reaction-products*, leading to an efficient *back-reaction* into the stable $\boxed{OH^-}$ configuration. If we supply reaction partners for the unstable products in the form of *F* centers, photo-decomposition of the $\boxed{OH^-}$ defect at room temperature *can* be achieved. We showed in the previous work[3] that the rate of the primary reaction (eqn 1) is completely temperature independent between 6 and 150 K. The *RT* result in Fig. 6(b), showing in a crystal with *F* centers the same reaction as at 150 K (Fig. 5) makes it very likely, that the *primary* OH^- *decomposition rate is temperature independent over the whole range* 0–300 K.

If small amounts of *F* light are added in the *RT* range, *F*-aggreatation of *F* centers into F_2, $F_3, \ldots$, complexes occurs (curve 3 in Fig. 6b). For low visible light exposure this is a completely independent process which does not affect the UV spectrum. Under heavier light exposure this simple situation changes, as measurements after full undispersed xenon lamp exposure show (Fig. 7). While the initial stages are identical to the one in Fig. 6 (*U* center formation and *F*-aggregation), prolonged heavy irradiation leads first to complete *F* center bleaching and later to the development of a broad band ascribed to colloids. In the UV range the initially formed high *U* band is transformed into a new broad band of unidentified nature at higher energies. This last result obtained under heavy irradiation at *RT* shows interesting new correlation effects between the photo-chemistry of the *F* centers and the oxygen + hydrogen defects. Without the OH^- doping, the same light irradiation into an (additively colored) *F* center system would lead in saturation to an equilibrium of *F* and "small *F*-aggregate centers" ($F_2, F_3, \ldots$), but never to colloids. In the presence of OH^- defects and UV light, the *F* centers can first be quantitatively converted into *U* centers and then by heavy UV-visible irradiation into colloids. A further exploration of these interesting effects and study into the nature of the new unknown UV band formed is beyond the scope of this work and will be pursued in an extra study.

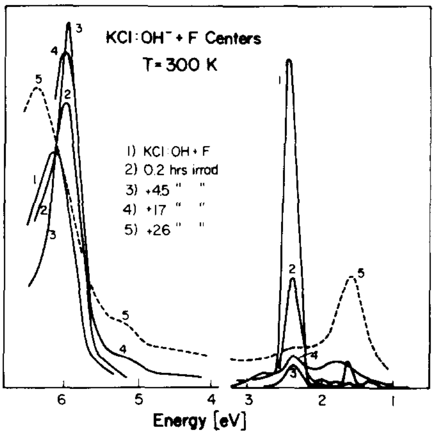

Fig. 7. UV and visible absorption spectra of an additively colored KCl:OH^- crystal before and after irradiation with undispersed light from a xenon lamp for various periods of time at 300 K.

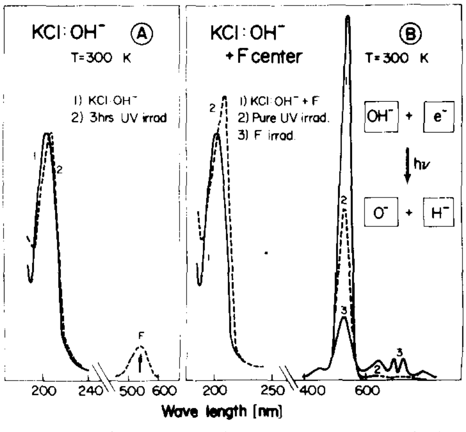

Fig. 6. UV and visible absorption spectra before and after UV (204 nm) and visible light irradiation at 300 K for an uncolored (a) and additively colored (b) KCl:OH^- crystal.

(4) *Summary on photochemistry and aspects of optical information storage*

Pure additively colored alkali–halide crystals are well known for their stability against a permanent bleaching of their coloration. Under visible light irradiation, these systems show the reversible $F \rightarrow F'$ reaction at low temperatures and the aggregation into complexes F_2, F_3, etc. at high temperatures (without appreciable loss of the integrated visible light absorption). When irradiating with only *visible* light into *F* center systems that also contain OH^- impurities, no new effects are observed. We again obtain the reversible $F \rightarrow F'$ conversion at low temperatures and the *F* center aggregation at high temperatures. These properties, however, change drastically in KCl:OH^- crystals if our irradiation contains UV light as we showed in this work. Under OH^- light irradiation, we were able to produce in a very broad temperature range an almost complete and irreversible destruction of

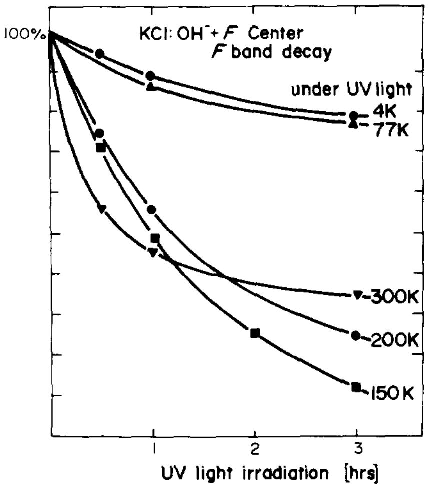

Fig. 8. F-band decay curves under UV light irradiation at various temperatures between 4 and 300 K for additively colored $KCl:OH^-$.

F centers and any visible absorption in the crystal under UV light irradiation.

In Fig. 8 we summarize the decay of the F center vs UV irradiation time for several temperatures of study. We see that this process has a small bleaching quantum efficiency at low temperatures. In this range, where basically all primary and secondary reaction products of the OH^- dissociation are thermally stable, the presence of the F centers has relatively little influence on these reactions, and therefore F centers become consumed only at small rates. Towards higher temperatures, the role of the F center as trapping or reaction-site becomes more and more decisive, leading to a strong increase in the rate of F center decay (Fig. 8). The presence of the F centers in the crystals changes completely the nature of the OH^- photo-chemistry in the 100–200 K range, while at *RT* any sizeable UV photo-chemistry of the OH^- takes place only in the presence of F centers.

This general behavior of additively colored OH^- doped crystals, *to make* UV *irradiation detectable by an effective and stable bleaching of visible coloration*, offers interesting possibilities for visible recording of UV light and for optical information storage. This general field has received in the last decade a lot of attention: three-dimensional "Bragg–angle holograms" have, for instance, been stored in large numbers by optical alignment of F_A centers in $KCl:Na^+$ crystals[8].

To demonstrate qualitatively in the simplest way these photochromic properties of the additively colored $KCl:OH^-$ crystals under UV irradiation, we produced some images in these crystals by a simple shadow process. The obtained contrast is remarkably high (60:1) and the images are stable at room temperature and normal light (containing no far UV components) over very long periods of time. Visible light exposure at room temperature only changes the color appearance of the crystal parts with coloration, without affecting much of the strong contrast to the part of the crystals bleached from coloration by UV light exposure. The thermal stability of the images is remarkable. Both the defects in the colored part (OH^- and additively colored F centers) and the defects produced by the UV bleaching-reaction in eqn (8) (substitutional H^- and O^- centers) are stable to high temperatures. Only under heating to temperatures above 650°C, a partial restoration of the coloration is observed. The created images therefore have an unusual high stability both against exposure to increased temperature and visible and near UV light.

(5) *Production of* U *centers on sites of low symmetry*

The possibility to create in our crystals $\boxed{H^-}$ defects by reaction of mobile hydrogen with an F center (eqn 8), allows the controlled production of "perturbed U centers." The F centers in the additive colored crystals can—prior to the UV irradiation—be mobilized by visible light irradiation at temperatures above −40°C. This leads to the formation of either the intrinsic F-aggregate centers ($F_2, F_3, \ldots$), or—in appropriately doped crystals—to the attachment of F centers to monovalent or divalent cationic impurities, forming F_A and F_Z centers. Under subsequent UV photo-dissociation of the OH^- defect, the hydrogen will therefore react with an F center in the F_2, F_3, F_A or F_Z complex, thus creating a corresponding $\boxed{H^-}$ defect at a site of locally reduced symmetry.

In order to demonstrate the feasibility of such a process, we converted in an additively colored $KCl:OH^-$ crystal, lightly doped with Na^+ defects, the F centers by visible light irradiation at 260 K into F_A centers (curve 1 in Fig. 9):

$$\boxed{e^-} + \boxed{Na^+} + h\nu \rightarrow \boxed{e^-\,|\,Na^+}. \qquad (9)$$

Proceeding with the OH^- photo-decomposition at 150 K (curve 2) and pulse annealing to room temperature (curve 3), we should have formed H^- defects neighboring Na^+ impurities ("U_A-centers") according to

$$\boxed{e^-} + \boxed{Na^+} + \boxed{OH^-} + h\nu + kT \rightarrow \boxed{O^-} + \boxed{H^-\,|\,Na^+} \qquad (10)$$

The success of this process can be checked by observing the $\boxed{H^-}$ local mode, which in the reduced (C_{4V}) sym-

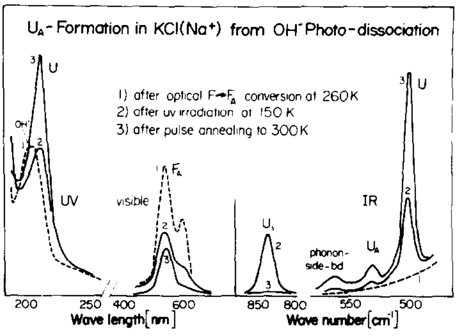

Fig. 9. U_A-Center formation in an additively colored $KCl:OH^-:Na^+$ crystal, obtained by the following treatments: (1) Optical $F \rightarrow F_A$ conversion at −15°C. (2) OH^- photo-decomposition at 150 K. (3) Annealing to room temperatures.

metry besides a $\boxed{\mathrm{Na}^+}$ defect should split into a doublet and singlet transition. Curve 3 in Fig. 9 shows indeed an additional local mode band at 530 cm^{-1}, which is due to the localized vibration of an $\boxed{\mathrm{H}^-}$ along the direction towards a (100) neighboring Na$^+$ ion[9]. This method of creating *U* centers with locally reduced symmetry out of *F* aggregate centers (which may even be optically aligned), appears to be very promising for further local mode studies.

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