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Low Temperature Bleaching of *F* Centers in Irradiated Alkali Halides

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The recovery of F centers after bleaching at liquid nitrogen temperature was studied in KCl and NaCl γ-rayed with various doses. The study of the effect of bleaching temperature and bleaching time on the recovery curves shows that the bleaching and recovery at liquid nitrogen temperature were due to the transfer of electrons from the excited state of F centers and from F' centers respectively without ionization. The recovery curves are also shown to be expressed by the summation of several exponentials. In KCl the recovery with the time constant of 2~4 min was most prominent for lower doses, whereas for higher doses the recovery appeared with the time constant higher than 50 min. It is concluded that there are two types of localization of F centers. The first type of localization seems to occur when vacancies are formed by radiation interacting with a point defect. The second type localization seems to arise from vacancies formed at dislocations, so that it can be observed only at higher doses. F centers in the first localization seem to be converted to colloids as the radiation dose increases. When the irradiation temperature is low, only the second type of localization was observed, the time constant for which is smaller.

1. Introduction

On the formation of color centers in alkali halides several mechanisms depending on irradiation temperature have been proposed[1)-7)]. It has been cleared out that at low temperatures color centers are formed in the bulk not depending on impurities nor dislocations[8),9)]. At room temperature, on the other hand, formation of color centers can be divided into two stages: in the first stage F centers are formed from vacancies initially present in the crystal, and in the second stage F centers are formed from newly created vacancies around dislocations[5),10)-12)].

Mechanism of vacancy formation at low temperature in the bulk of crystal is of Varley type[2),3),6)]. Formation mechanism around dislocation at room temperature has been discussed by Mitchell, Wiegand and Smoluchowski[5)] and also by Bauer and Gordon[7),13)]. Both of them assume that negative ion vacancies are formed at the core of dislocations and escape from there. Mitchell *et al.* analysed the formation curves and concluded that F centers are localized around dislocations.

Bron[4)] and present authors[15)] studied the bleaching near room temperature of F centers of KCl formed by irradiation at room temperature, and concluded that F centers formed in the second stage of irradiation are much more stable to F light illumination than those formed in the first stage of irradiation. The present authors also came to conclusion that complex centers are formed only when F centers and other defects are highly localized[15)].

Markham, Pratt, and Mador[16)] have studied low temperature bleaching of F centers in KBr and KCl, and found that bleaching by illumination and subsequent recovery occur in specimens colored at room temperature by irradiation, and they do not occur in specimens colored by irradiation at liquid nitrogen temperature nor in specimens colored additively. They concluded that color centers formed at room temperature do not distribute uniformly, and they ascribed the bleaching to transfer of electrons from excited state of F center to another F center by tunneling (F' centers are formed), and the subsequent recovery to transfer of electrons from F' centers to negative ion vacancies[17)]. Although the detailed mechanism of electron transfer is not clear, it is evident that the bleaching and recovery at low temperatures depend on the distribution of F centers.

In order to clarify the detailed mechanism of color center formation in the second stage, it is necessary to know more about localization. The present investigation is undertaken to make clear how the degree of localization changes with various conditions of irradiation by utilizing the bleaching experiment at low temperature. The effects of radiation dose, plastic deformation and irradiation temperature on bleaching at liquid nitrogen temperature were studied. Two types of localization were found, and the models for each localization are presented.

2. Experimental Details

The specimens were obtained from an ingot of KCl and NaCl purchased from Harshaw Chemical Co.. They were irradiated in the Co^{60} cave of JAERI up to the dose of 2×10^9 r. For the measurement of effect of irradiation temperature specimens were irradiated by x-rays for convenience. The applied voltage to x-ray tube was 50 kv, and the current was 17 ma. Plastic deformation was done up to 2% by a compression machine.

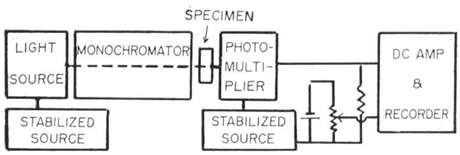

Fig. 1. Measuring circuit.

Measurement of bleaching and recovery was done at liquid nitrogen temperature with the apparatus as shown in Fig. 1. The specimen was illuminated by F light through the monochromator with the slit width of 2 mm. After bleaching, the slit width was changed to the normal operating width and the change of transmitting F light was measured. The intensity of bleaching light 10^{14} photons/cm^2 sec, and that of measuring light was 1/100 smaller. It should be noted that intensity of light used here both for bleaching and measurement is considerably smaller than that used by Costikas and Grossweiner, whose work mainly dealt with photo-ionization[18]. The apparatus is constructed to amplify only the change of transmitting light: photomultiplier output due to the transmitting light before bleaching was compensated by current from a battery. The power supplies for light source and photomultiplier were well regulated.

In order to obtain the change Δn_F of F center concentration through the change in transmitting light, care should be taken that the bleaching light attenuates as going into the specimen. The change ΔI in transmitting light due to bleaching with incident light J_0 can be expressed as

$$\frac{\Delta I}{I_0(d)}=\sigma_F J_0\{1-\exp(-\sigma_F n_F{}^0 d)\}\frac{\Delta n_F}{n_F{}^0} \qquad (1)$$

where σ_F is the cross section of F centers for photons, d is the thickness of specimens, and $I_0(d)$ and $n_F{}^0$ are the transmitting light and concentration of F centers, respectively, before bleaching.

3. Experimental Results

As the thermal ionization energy of electrons in F' centers is 0.42 ev for KCl and that for NaCl is slightly larger, thermal ionization from F' centers is not expected at liquid nitrogen temperature. Therefore, measurement was done on the transition of electrons from F' centers namely, recovery of F center after F bleaching, which seems

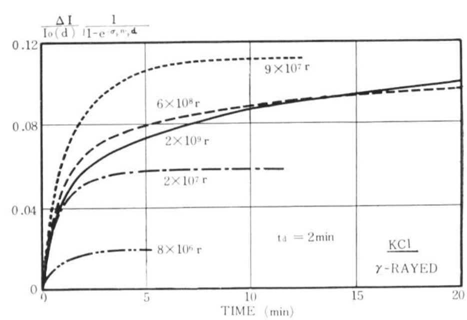

Fig. 2. Recovery curves of F centers in KCl colored by γ-ray after 2 min bleaching with F light at 79°K.

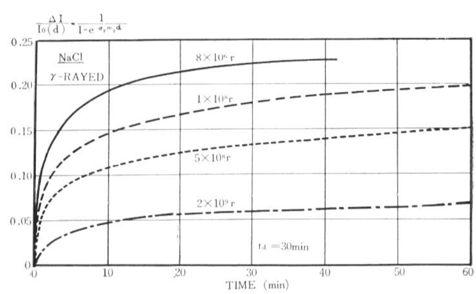

Fig. 3. Recovery curves of F centers in NaCl colored by γ-ray after 30 min bleaching with F light at 79°K.

to be pure tunneling phenomenon. Although a little ionization from the excited state of F center seems to occur, it was observed that after repeating the bleaching several times all of the bleached F centers recovered.

The typical recovery curves of F centers after F bleaching at 79°K are shown in Figs. 2 and 3 for KCl and NaCl, respectively, colored by γ-rays to various doses. The similar curves for decrease of F' centers were also obtained. The bleaching time is 2 min and 30 min, respectively. It should be noted that the recovery occurs within 5 min for KCl γ-rayed to 2×10^7r, but slow recovery is observed for KCl γ-rayed to higher doses. In NaCl, the slower components of recovery, which appeared in KCl at higher doses, could not be observed in the dose range up to 2×10^9 r. It is also clear that the amount of recovery decreases as the radiation dose increases. The recovery curves for additively colored KCl were also studied, and in this case recovery occurred only within 2 min.

In order to know if the bleaching and recovery observed is due to ionization or not,

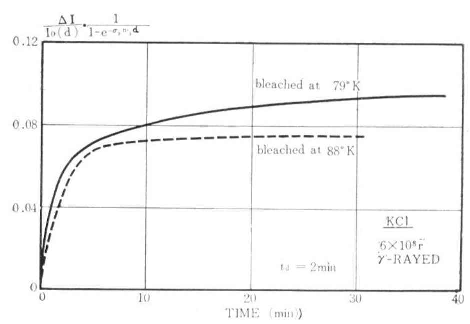

Fig. 4. Recovery curves of F centers in KCl γ-rayed to 6×10^8r after 2 min bleaching with F light both at 79°K and 88°K.

the temperature dependence of the recovery curves was studied. Fig. 4 shows a result of bleaching temperature dependence of recovery curve for KCl γ-rayed to 6×10^8r. It is seen that the slower recovery disappears as the bleaching temperature increases. The recovery curves for different bleaching time intervals were also studied. The result for radiation dose of 6.4×10^8r is shown in Fig. 5. It is seen from this result that the recovery process is composed of several components: the slow recovery is prominently enhanced with increasing bleaching time interval.

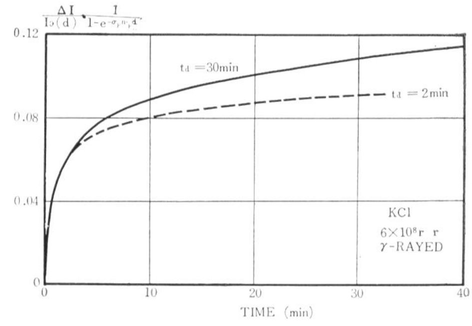

Fig. 5. Recovery curves of F centers in KCl γ-rayed to 6×10^8r after both 2 min and 30 min bleaching with F light at 79°K.

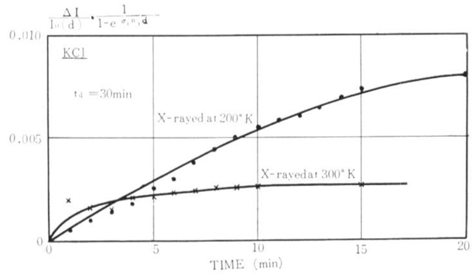

Fig. 6. Recovery curves of KCl x-rayed both at 200°K and 300°K. After coloration the specimens were bleached at 79°K for 30 min.

Fig. 6 shows the effect of irradiation temperature on the recovery curves. The specimens were irradiated in this case with x-rays for 3 hours both at 200°K and at room temperature. After irradiation the specimens were cooled to liquid nitrogen temperature and illuminated by F light. The recovery curves after illumination for both cases are shown in the figure. In KCl colored at low temperature the rapid recovery was not observed as in the case of room temperature irradiation, and the time constant for slow recovery increases.

4. Discussion

In discussing the bleaching experiment it should be noted that the rate of transfer of electrons both from excited state of F centers to F' centers and from F' center to the ground state of F center depends strongly on the distance between F centers[19]. Therefore we assume for simplicity that the excited electron goes to the nearest F center

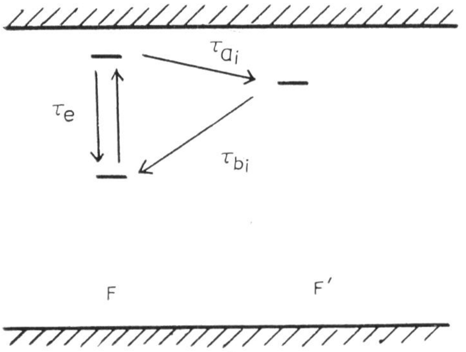

Fig. 7. Cycle of electron transfer.

with the highest probability, and returns to the original vacancy. Thus we can take a simple cycle of electrons as shown in Fig. 7. Relaxation time for each process is expressed as shown in the figure. The change in F center concentration can be calculated by solving kinetic equations. The result for recovery curve of F center concentration after strong F light bleaching for time interval t_d is

$$\frac{\Delta n_F}{n_F{}^0}=\sum_i \frac{\tau_{b_i}}{1+\frac{\tau_{a_i}}{f_i\tau_e}}\{1-\exp(-t_d/\tau_{b_i})\}\exp(-t/\tau_{b_i}), \quad (2)$$

where summation is done for F centers having their neighbor at different distances, and f_i denotes the portion of F centers having its neighbor at the distance giving the relaxation time τ_{b_i}. In deriving Eq. (2) approximations were used that $1/\tau_e \gg 1/\tau_{b_i}$, $\sigma_F J_0$: the value of τ_e obtained by Swank and Brown[20] is 10^{-6} sec at liquid nitrogen temperature, and τ_{b_i} obtained in the present experiment is larger than 10 sec and $\sigma_F J_0 \approx 10^{-1}\text{sec}^{-1}$. From the obtained value of $\Delta n_F/n_F{}^0$ and τ_{b_i}, it is easily shown that

$$1+\frac{\tau_{a_i}}{f_i\tau_e}\approx 10^3.$$

As $f_i<1$, the value of τ_{a_i} is much smaller than τ_{b_i}. Therefore, the mechanism of transfer from the excited state of F center may be of different nature from that of transfer from F' centers. Eq. (2) can be rewritten as

$$\frac{\Delta n_F}{n_F{}^0}=\sum_i \frac{\tau_{b_i}\tau_e}{\tau_{a_i}} f_i\{1-\exp(t_d/\tau_{b_i})\}\exp(-t/\tau_{b_i}). \quad (3)$$

It can be verified by the experimental results shown in Fig. 5 that the recovery curves obtained in the experiment can be expressed by the summation of the exponential terms as shown in Eq. (3). As the magnitude of each exponential term contains the factor $1-\exp(-t_d/\tau_{b_i})$, it is easily seen that with increasing bleaching time t_d the magnitude of the slow time constant term increases. Moreover as shown in Fig. 4, the large τ_{b_i} components decrease as the bleaching temperature increases. This result can be explained if one considers that with increasing temperature, the life time of electrons at the excited state of F center decreases due to thermal ionization, as shown by Swank and Brown. With decreasing life time at the excited state, the transition of larger τ_{a_i} becomes improbable.

The division of the recovery curves into components was attempted by a trial-and-error method to get the best fit for the curves shown in the figures and also their derivatives. In KCl for smaller doses than 9×10^7r the distribution of τ_{b_i} has a maximum around 2~4 min, and as the doses become higher the components of τ_{b_i} around 100 min begin to increase, and this time constant decreases with increasing dose.

It is seen from Eq. (3) that the magnitude of each component is proportional to $(\tau_{b_i}/\tau_{a_i})f_i$, and if we assume that τ_{b_i}/τ_{a_i} does not depend on the distance between F centers, this magnitude is proportional to f_i: the portion of F centers having its neighboring F centers at the distance corresponding to the recovery time τ_{b_i}.

It should be noted here that in the model discussed by several authors[5),13)] the vacancies are assumed to be formed at the core of dislocation and to escape from it, and F centers are formed after these vacancies trap electrons. In this case we can take an effective volume in which F centers can be formed, and it is expected that in small doses F centers are formed in this volume sparsely, and with increasing dose the distance between F centers decreases.

The experimental results obtained are inconsistent with this expectation: the recovery with small time constant appeared in the dose of 8×10^6 r, which increased till the dose increases to 9×10^7 r, and above that dose recovery with large time constant appeared.

Two explanations are possible for this result. (1) that F centers are formed at dislocation core and radiation helps them to diffuse from the core, or (2) that there are two agents for vacancy formation: one is point defect and the other is dislocation. If we assume that two vacancies are formed from a certain point defect by its interaction with primary radiation effect, then vacancies formed will be located closely to each other. When the vacancies are formed from dislocation, however, the mean distance between vacancies decreases with increasing dose, and this type of localization can only be detected by bleaching experiment when the radiation dose is large enough.

The second explanation seems to be probable. The reason is as follows. (1) The distribution curve for τ_{b_i} is the same for rapid component through the radiation dose studied, and slower component seems to be added independently. (2) It was observed that plastic deformation does not affect the rapid component appreciably. Therefore it is tentatively assumed that in the second stage F centers are formed in part at point defects, which results in most concentrated F centers, and that the other part of F centers are formed at dislocation, which become more concentrated as the radiation dose increases.

In this connection it should be noted that especially in NaCl colloids are formed as the radiation dose increases more than 10^8 r, as pointed out by Compton[21]. In KCl colloids are formed at still higher doses, and it is interesting here to point out that the decrease in rapid component of recovery occurs more prominently in NaCl. It is natural to consider that the concentrated F centers are converted to colloid as the radiation dose increases. As shown by Compton colloids are formed only when crystals contain OH^-. Therefore it may be probable that the agent causing concentrated F centers is OH^-. Studies on this point are being done.

When the irradiation is done at lower temperatures no rapid component is observed and the time constant for the slower component is small. This suggests that the low diffusivity of defects at low temperature makes F centers more concentrated around dislocation. More study should be done in order to get complete models.

Acknowledgement

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DISCUSSION

Smoluchowski, R.: Do you have evidence that F centers interact at distances larger than 3 or 4 atomic radii?

Itoh, N.: If we assume that most concentrated F centers are separated at the distance of 2∼3 atomic radii, in the second type of localization, the distance between F centers should be 4∼6 atomic distances, because the time constant for the bleaching in the latter case is 50 times as large as that in the former case.