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**論　文**

# Distribution of Tritium Produced in LiF by Neutron-Irradiation

Osamu TAKAYASU, Yoshiki NAKANO,
and Toyosaburo TAKEUCHI

Faculty of Science, Toyama University, Toyama 930, Japan

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## ABSTRACT

This study is concerned with the autoradiographical study on cohesive sites of tritium on the surface layer of neutron-irradiated LiF. Many linear lines were found in the autoradiographs, but some of these lines were not in the microphotographs. These results were discussed with reference to the studies on the temperature programmed desorption of tritium and those on the absorption u.v. spectra of the irradiated LiF. These results indicate that tritium accumulates preferentially on the lattice imperfections of step-edges of LiF.

## INTRODUCTION

Tritium and helium produced by $^{6}Li(n,\alpha)^{3}H$ reaction have energy, 2.7 MeV for tritium and 2.1 MeV for helium respectively. It is expected, therefore, that large quantities of fresh lattice defects are produced in the neutron-irradiated LiF by these fission products. Lattice defects have been proved as the cohesive sites of impurities as well as their pass ways in metals.[1-3] This paper is concerned with the autoradiographical study on cohesive sites of tritium produced in the LiF irradiated with neutrons at low temperature. The autoradiographical images were compared with those of microphotographical images of the same surface. The changes in u.v. spectra and radioactivity of the irradiated LiF due to the elevation of temperature were observed.

## EXPERIMENTAL

Single crystals of LiF were provided by Harshaw Chemical Co. They were

irradiated with neutrons in JRR-1 or 2. A liquid-nitrogen temperature was used during the irradiation to avoid the elevation of temperature of the sample. The radiation dose was $10^{18}$ nvt. Prior to the autoradiography, the sample was fractured along a cleaveage plane at room temperature in order to obtain the fresh surface. Stripping film, Fuji ET-2F, was used for the autoradiography. The corrosion of the sample could make small by using the saturated solution with LiF instead of pure water as floating solution, in which the film emulsion was floated with subsequent contact with the sample. The sample which was contacted with the film emulsion was wrapped with black paper together with silica gel and kept at 4-5°C in a freezer for two weeks.

In order to clarify the crystal structure, the irradiated sample was etched in the solution made with conc. HF, glacial HAc(1 : 1) and pinch of $FeF_3$ for 90 s at 30°C.[4] Etch pits appeared on the surface were observed by a microscope.

The absorption spectra of the irradiated samples were recorded with a Hitachi UV-220 spectrophotometer to study changes in lattice defects. The samples were treated at various temperatures for one hour before use.

The amount of tritium evolved from the LiF was measured in the presence or the absence of hydrogen by heating the sample stepwisely upto 400°C in vacuum system which can keep the pressure to be $10^{-6}$ Torr. The measurement of tritium accumulated in gas phase and that on the surface were carried out by means of a radio-gas chromatograph and a $2\pi$-counter respectively.

## RESULTS

Figs. 1 and 2 are the autoradiographs of the surface. In these figures, (a) is the autoradiograph, and (b) and (c) are the microphotographs of the same surface after the autoradiograph was taken and that after the sample was etched respectively. The pattern in (c) consists of numerous dislocation etch pits, which exist parallel to (100) direction. The autoradiograph (a) is composed of many lines. However, some of these lines can be recognized in (c) but not in (b), and some of them can be recognized neither in (b) nor in (c). Fig. 3 shows the autoradiograph taken after the etching. Unexpectedly, no pattern which corresponds to etch pits was recognized.

Fig. 4 shows the absorption spectra of the irradiated sample which was annealed at various temperatures. Only two absorption bands at 240 and 400-470 nm were observed in the sample which was kept at room temperature after the irradiation.

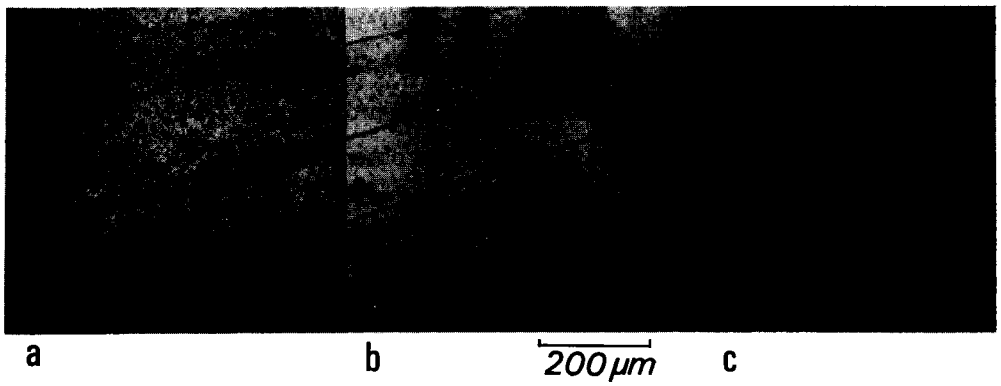


Fig.1 Autoradiograph and microphotographs of a surface of the neutron-irradiated LiF. Neutron dose ; $7.9_{x}\ 10^{18}$ nvt, a ; autoradiograph (exposed 14 days), b ; microphotograph of the same surface after taking the autoradiograph, c; microphotograph of the same surface after the etching.

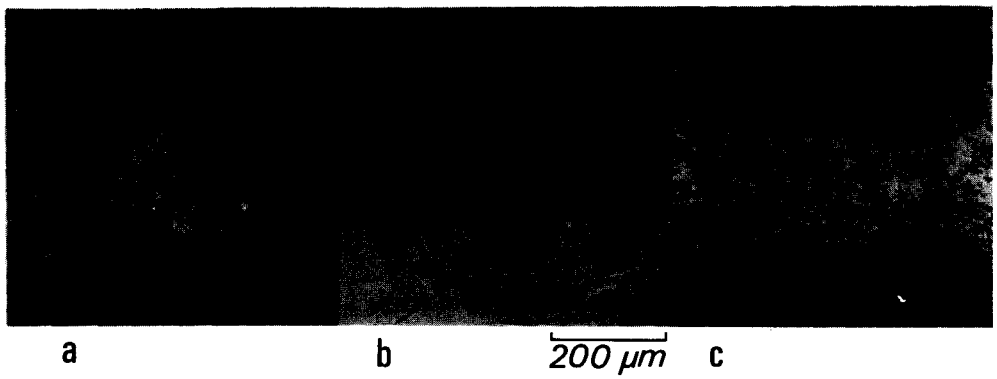


Fig.2 Autoradiograph and microphotographs of a surface of the neutron-irradiated LiF. Neutron dose ; $7.9 \times 10^{18}$ nvt, a ; autoradiograph (exposed 14 days), b ; microphotograph of the same surface after taking the autoradiograph, c ; microphotograph of the same surface after the etching.

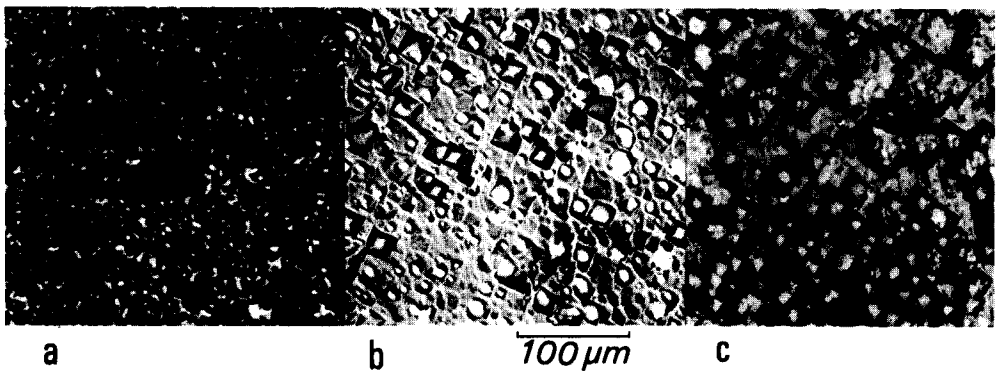


Fig.3 Autoradiograph and microphotographs of the surface of neutron-irradiated LiF after the etching.
Neutron does ; $9.9_{x}\ 10^{16}$ nvt, a ; autoradiograph (exposed 37 days), b ; c ; microphotographs of the surface before and after the autoradiograph was taken.

The intensities of these bands decreased gradually as the annealing temperature increased. The noticeable band at 295 nm appeared at 200°C, but it shifted toward the shortwave side, 270 nm, when the temperature approached to 370°C. Before the appearance of this band, new band at 415 nm was observed near 200°C, and the band at 340 nm was observed at 280°C.

The amounts of tritium appeared in the gas phase and that on the surface of the irradiated sample at various temperatures are shown in Fig. 5. Both amounts changed markedly at above 300°C. The coexistence of hydrogen with the sample did not influence on the evolution.

## DISCUSSION

The displacement of atoms of nondisintegrated Li and F in the sample would occur by the large energy, 2.7 MeV for tritium and 2.1 MeV for helium, generated by $^{6}Li(n,\alpha)^{3}H$ reaction. Vacancies of $Li^{+}$, tritium atoms and helium atoms produced by the reaction would readily migrate in the lattice of LiF, as had been reported elsewhere,[5,6] such as the following hydrogen centers: $H_s^-$ and $H_s^0$. In addition, tritium atoms can exist as interstitial atoms.[7]

The activation energy of volume diffusion of tritium in the irradiated LiF is in the

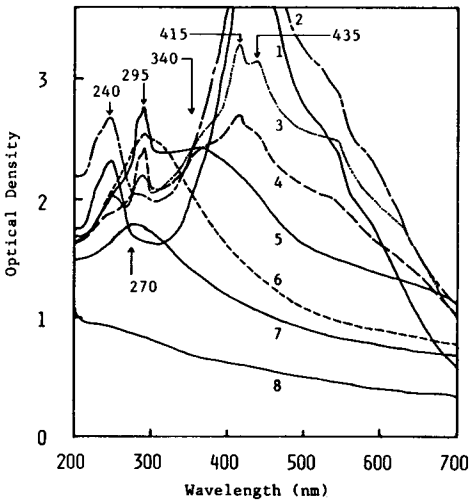


Fig. 4 The optical absorption spectra of the neutron-irradiated LiF heated at various temperatures.
1——R.T.; 2– – –100°C; 3·····200°; 4– – –240°; 5——280°; 6– · – ·320°; 7——370°; 8——420°

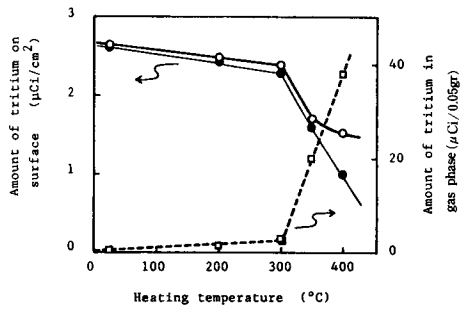


Fig. 5 The amounts of tritium evolved from the neutron-irradiated LiF at various temperatures.
○ : The amount of tritium on the surface of the LiF which was heated in the presence of hydrogen, ● : The amount of tritium on the surface of LiF heated in vacuum. □ : The amount of tritium in gas phase. The LiF was heated in the presence of hydrogen.

range of 40-50 Kcal/mol.[8-10] These values are based on the studies at more than 200°C.

At near 200°C, the diffusion of point defects and interstitials is readily accelerated and the structure is changed as can be understandable in the study on the u.v. spectra. At this temperature, intensity of the band at 400-470 nm decreased and that at 240 nm disappeared. On the contrary, the new band at 295 nm appeared. The bands at 240, 440, and 415 nm correspond to F, $F_2$, and $F_5^+$ centers respectively.[11] Politov et al. reported that the bands at 295, 340, and 465 nm correspond to the formation of atomic, quasicolloidal, and colloidal particles of lithium respectively.[12] However, the band at 465 nm did not appear in our study. The evolution of tritium occured, when the band at 295 nm shifted toward the shortwave side of 270 nm. This finding suggests that tritium exists being stabilized by atomic lithium. One may assume, therefore, that the disappearance of tritium makes the atomic lithium unstable, and promotes the rearrangement of lithium atoms. Probably, the formation of crystallites of lithium or LiF would occur.

The temperature employed in the autoradiographical study was below 30°C. The activation energy of the diffusion of metal ions suggests that the rate of the structural change of the irradiated LiF at this temperature is far small, ca. $10^{-5}$, in comparison with the case treated at 200°C. However, the diffusion on the surface even at room temperature can not be completely ignored, because the activation energy of surface diffusion is smaller than that of volume diffusion.[13] It may be concluded, therefore, that a part of tritium diffuses from the interior to the surface along lattice imperfections and fixes at the stable positions of the surface, such as the corners of steps, probably the edge of $F^-$(111) plane or the crystallites of lithium. Several types of step-edges of crystal are defined in regard to the structure of metal surface : one-atom-height steps, multiple height steps composed of wide step-terrace, and hill and valley structure.[14] Bernasek and Somorjai[15] found that the exchange reaction of hydrogen with deuterium does not take place on the (111) crystal face of platinum but takes place on the high Millaer index stepped surface, and that kink site in steps is effective in breaking of H-H bond. The previous study[16,17] by means of electron-microscope autoradiograph proved that tritium accumulates preferentially on step-edges on neutron-irradiated nickel covered with lithium. Similar explanation can be given for ionic crystals. It would be rational that the edge of the so called "one-atom-height steps" of $F^-$(111) is also active in these structures for the capture of tritium.

The disagreement between the patterns of (a), and those of (b) and (c) in Figs. 2 and 3 would be attributed to the number of one-atom-height step in the step on the

surface. The step could not be recognized in (b) and (c), when the number of the one-atom-height step is small, even if the image of lines could be recognized in the autoradiograph. On the other hand, some straight lines in the autoradiograph (a) were not recognized in (b) but recognized in (c), when these lines in (a) can be attributed to the tritium accumulating preferentially on dislocations.

## ACKNOWLEDGMENT

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