PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT III, 1963

Direct Observation of Crystal Imperfections in KCl Single Crystal due to Electron and X-Ray Irradiation

T. HIBI, K. YADA AND Y. KAWAMATA
Research Institute for Scientific Measurements
Tohoku University, Sendai, Japan

Observations were made electronmicroscopically of crystal imperfections caused by electron and x-ray irradiation in thin KCl single crystals made by three different methods. In KCl crystal made from its water solution, loop structures appeared and disappeared and then small cubic cavities appeared under weak electron irradiation, while large cubic cavities appeared directly under intense electron irradiation. In KCl crystal made by electrolytic etching, parallel pair dislocation lines always appeared besides loop structures and then disappeared under weak electron irradiation, while small bright specks appeared under intense electron irradiation. In KCl crystal made by water etching, dislocation loops first appeared and then loop structures appeared and then disappeared under weak and also intense electron irradiation. In x-ray irradiated KCl crystal made from water solution, loop structures and dislocation lines appeared and then disappeared, while large cavities were rarely observed under intense x-ray irradiation. The mechanism of coagulation of vacancies is discussed.

1. Introduction

Direct observations of the thin metallic foil were made electronmicroscopically by many workers[1] for the study of crystal imperfections. However, no report has been made on such a direct observation of alkali halide crystal. We succeeded in making thin KCl crystals from its water solution by vacuum drying method[2] and from its bulk crystal by chemical and electrolytic etching methods.[3] Therefore, crystal imperfections caused by electron and x-ray irradiation in KCl single crystals prepared by these methods were directly observed by means of an electronmicroscope and electron diffraction.

2. Experimental Method

Thin KCl single crystals having {100} base plane were used in the experiments. Successive observations of the specimens irradiated with the electron beam of electronmicroscope or irradiated with x-rays were made under HS-6 electronmicroscope operating at 50 kv. The electron diffraction pattern of the selected area and dark field image were also obtained with the same instrument.

The intensity of electron irradiation was controlled by changing the current of the electronmicroscope condenser lens. In the case of x-ray irradiation, x-ray intensity of 35 kv, 7∼15 ma was used and the distance between Co-target and the specimen was always about 3.5 cm. After x-ray irradiation, the specimen was observed under a very weak electron beam (about 150 $\mu a/cm^2$) of the electronmicroscope to avoid any electron irradiation effect.

To examine the effect of the rise in temperature on the specimen, an electric furnace was prepared in the electronmicroscope. Replica technique was also used in examining the surface structure of the specimen. A usual Cr-shadowed carbon replica was tried, and also a SiO one-step replica was prepared by evaporating SiO in the specimen chamber of electronmicroscope without removing and exposing the specimen to the air. The crystal thicknesses were estimated from the shadow lengths cast by metallic shadowing.

3. Experimental Result

(*a*) *Observations of thin KCl crystal made from water solution under electron irradiation.*

A typical example of the process of changes caused by weak and intense electron irradiation is shown in Fig. 1. Under weak electron irradiation,* pair-loops appeared, as shown in (a), showing a perfect net-like pattern, as shown in (a'). At a certain stage of weak irradiation, their development ceased and

* The current density of weak electron irradiation on the specimen was of the order of several hundred micro-amperes per cm^2.

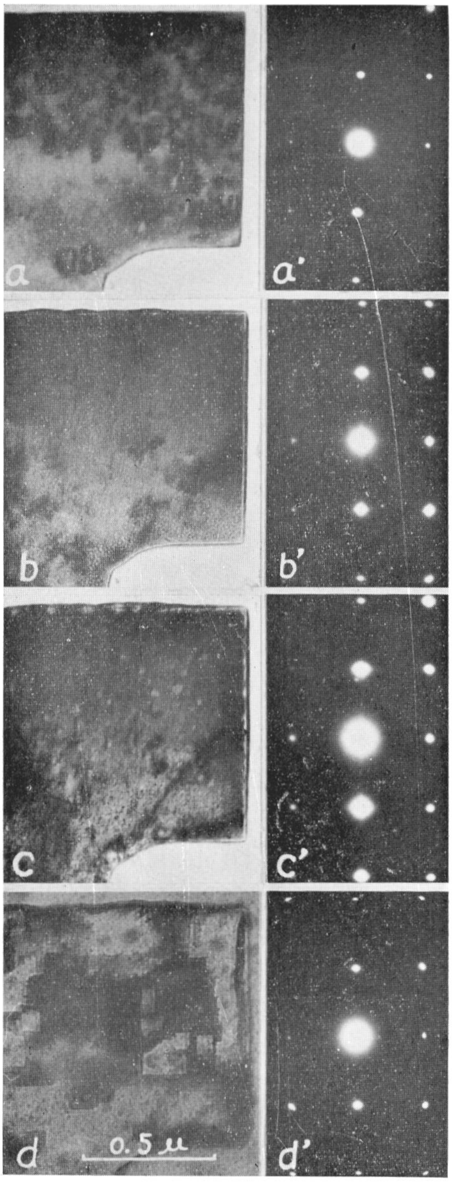

Fig. 1. A typical example of the successive changes due to weak and intense electron irradiation.

then the loops disappeared (b), showing streaks of electron diffraction spots (b'). A large number of small bright specks then appeared over the whole crystal (c) and the streaks of the electron diffraction spots became pronounced (c'). At this stage, by changing to intense electron irradiation,* the bright specks changed to large squares, as shown in (d), showing a perfect net-like pattern again (d'), while, by continuing weak irradiation, the crystal gradually changed to the polycrystal having grain boundaries.

On the other hand, under intense electron irradiation from the beginning, large bright squares whose edges were arranged in ⟨100⟩ directions appeared directly without any stage showing loop structures. Similar large bright squares were also observed recently by Möllenstedt and his co-workers[4] in the KCl crystal made by their new method. It is very important that the behavior of the change caused by electron irradiation in KCl crystal depends on the electron beam intensity.

In order to know the origin of the process of appearance and disappearance of loop structures, the effect of the rise in temperature by 200°C on the specimen was examined under the electronmicroscope. The loop structures which appeared in the early stage of weak irradiation disappeared completely after a 30 miniute heat treatment. Therefore, it was found that the effect due to the rise in temperature is inverse of the effect of weak irradiation in the stage of the appearance of loops; *i.e.*, the stress concentrates in the crystal with weak electron irradiation.

However, in the stage in which the loop structures due to weak irradiation begin to disappear, the effect induced by the temperature rise of 200°C is different from the abovementioned effect. That is, the loop structures in this stage also disappeared by the heat treatment, but large numbers of small bright specks appeared over the whole crystal and the streaks of electron diffraction spots appeared along ⟨100⟩ directions. Therefore, in the process of disappearance of the loop structures, the heating effect of the specimen due to electron irradiation was more predominant than that of stress concentration.

From the observation of the loop structure by means of replica and dark field methods, it was found that the loop structures are formed not on the crystal surface but in the crystal and the contrast of loops was due to Bragg diffraction at the crystal defects considered by Möllenstedt[5] to be voids having convex lens-like shape.

Pashley[6] reported that in the case of the thin metallic film, the appearance of the loop

* The current density of intense electron irradiation on the specimen was of the order of about ten thousand micro-amperes per cm².

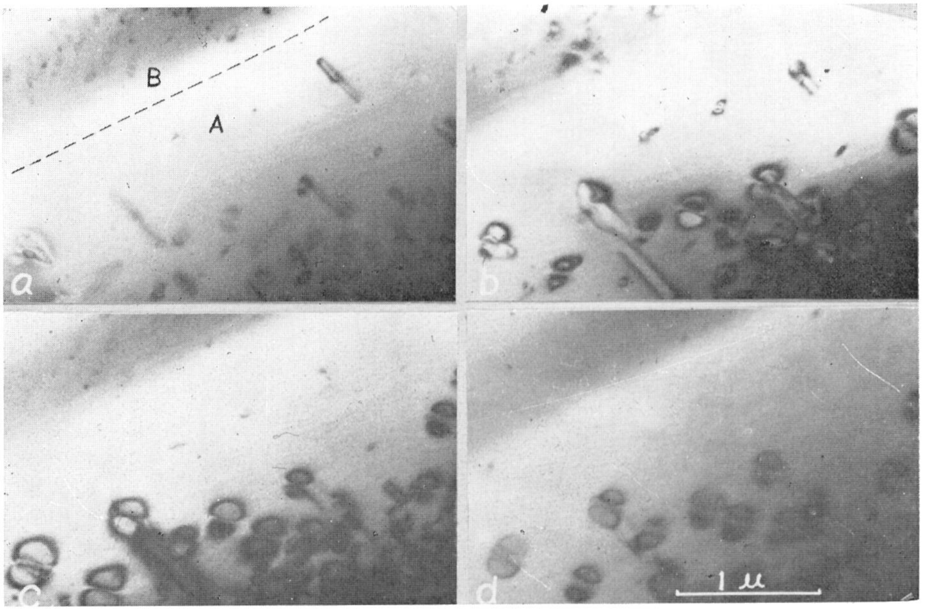

Fig. 2. The changes due to weak electron irradiation in KCl crystal made by electrolytic etching method.

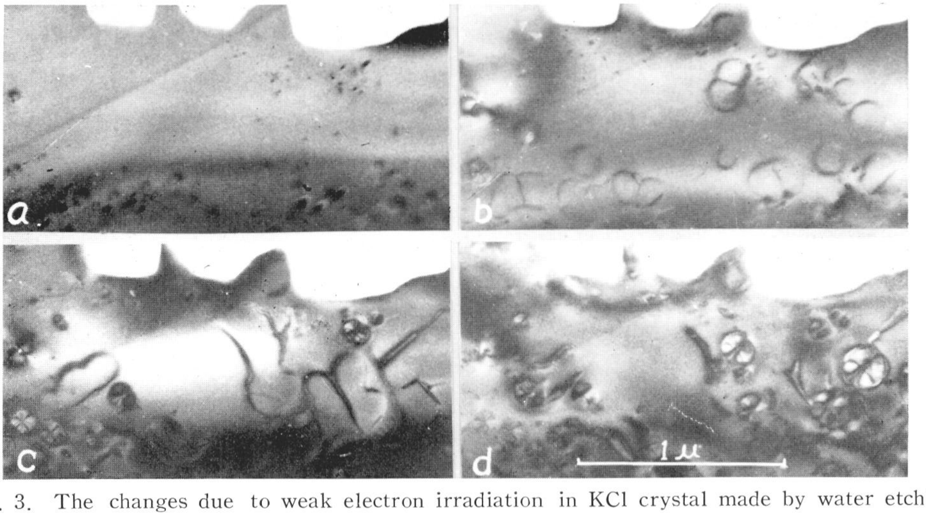

Fig. 3. The changes due to weak electron irradiation in KCl crystal made by water etching method.

structures was caused by a bombardment on the specimen of ions in the vicinity of the electron gun of the electronmicroscope. To confirm which is more predominant, the electron irradiation or ion bombardment in the case of KCl crystal, a carbon film (200~300 Å thick) mounted on a specimen grid was inserted in the position of condenser lens aperture of electronmicroscope to absorb the ion beam. As a result, it was found that the loop structures appeared and then disappeared only by electron irradiation without the function of ion bombardment.

The electron image of small bright specks was observed under high magnification. As a result, it was found that the small bright specks were the squares* whose edges were arranged in ⟨100⟩ directions. It was also known that these bright small squares revealed the presence of small vacant cubic cavities in the crystal by means of dark field method. Therefore, it was confirmed that the cause

* The smallest observable size of these squares is about 40Å in side length.

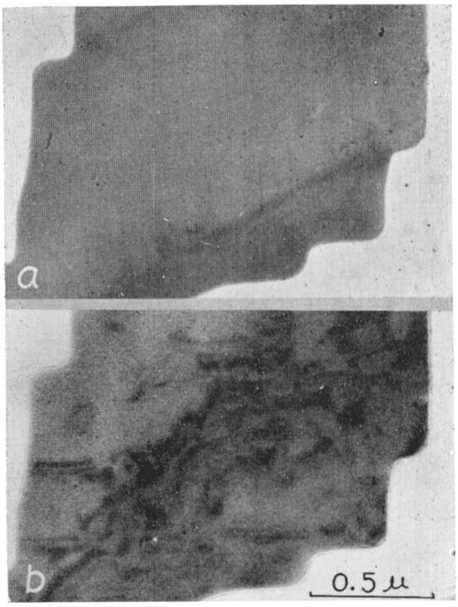

Fig. 4. The change due to x-ray irradiation in KCl crystal made from water solution; (a) original state, (b) the state after x-ray irradiation at 35 kv, 15 ma.

of the streaks in the electron diffraction spots were attributed to the presence of very small cubic cavities.

From the examination of a large bright square, by means of replica and dark field methods, it was found that these squares were formed not on the crystal surface but in the crystal and were vacant cube-like cavities.

Accordingly, the change in electron irradiated KCl single crystal made from water solution can be attributed to the following mechanism. With weak electron irradiation, very small voids (about 10 Å in height) first appear in the crystal and become larger by the aggregation of vacancies. The growth of the voids presently ceases at the time when the maximum height is about 100 Å and maximum diameter is about 2,500 Å. Then the contraction of the voids begins by the escape of vacancies and the voids presently disappear. The escaped vacancy aggregate and small cubic cavities whose edges are arranged in ⟨100⟩ directions are created here and there in the crystal, showing pronounced streaks in the diffraction pattern. Through the continuance of weak irradiation, the small cavities increase in number and the crystal gradually changes to polycrystal having grain boundaries. Otherwise if an intense irradiation is given at this stage, small cubic cavities aggregate one another and become large cavities. The surrounding parts revert to perfect single crystal, as before irradiation.

(*b*) *Observations of thin KCl crystals made by electrolytic etching and water etching-methods under electron irradiation*

Successive changes caused by weak electron irradiation in KCl crystal thinned by electrolytic etching method are shown in Fig. 2. In the early stage of weak irradiation, loops appeared as shown in (a). The loops in the region A developed gradually as shown in (b) and (c) and then continued to disappear very slowly (d), though the loops in the region B were easy to appear and disappear. Besides these loops, parallel pair dislocation lines always appeared and developed along ⟨100⟩ directions, as shown in region A of (a), (b) and (c) and then disappeared (d), though such lines rarely appeared in the specimen made from water solution.

When the KCl crystal thinned by electrolytic etching was irradiated with intense beam, small specks appeared over the whole crystal and streaks in the diffraction pattern also appeared. However, large bright squares could not be observed.

Successive changes caused by electron irradiation in the KCl crystal thinned by water etching method are shown in Fig. 3. In the early stage of weak irradiation, dislocation loops first appeared, as shown in (a) and developed (b) and then loop structures due to voids appeared (c), (d).

Neither small specks nor large bright squares could be observed even in the case of intense electron irradiation.

From these results, it is noted that the changes in KCl crystal are different from one another with the crystals made by different methods and strongly dependent on the electron beam intensity on the crystal.

(*c*) *Observation of KCl crystals made from water solution under x-ray irradiation*

The change due to x-ray irradiation in KCl crystals exposed to the air and in vacuum was observed. Fig. 4 shows the results obtained from the specimen irradiated with x-rays at room temperature in the air. After the original state (a), loop structures appeared with x-ray irradiation as shown in (b) and then disappeared. The density and the size of the loops were smaller than those in the case of electron irradiation. Besides the loop structures, parallel pair dislocation lines always appeared along ⟨100⟩ directions in the early stage of x-ray irradiation, as shown in (b). When the specimen was placed in vacuum, loops appeared and disappeared with x-ray irradiation, however, dislocation lines did not appear.

In the case of x-ray irradiation, small bright specks did not appear, unlike the case of electron irradiation. However, large bright squares rarely appeared with intense x-ray irradiation in air or in vacuum though they were slightly obscure. Therefore, it is noted that the creation of large bright squares is limited to the KC1 crystal made from water solution.

4. Conclusion

As described above, the formation of imperfections in KC1 crystal strongly depends either on the intensity of irradiation or on the method of preparation of the specimen. Moreover, the thickness of the crystal plays an important role. In the case of crystal thinner than about 400 Å the loop structures are hardly observed with electron or x-ray irradiation. This result may be explained from the fact that vacancies created in very thin crystals escape easily from the surface. In the case of crystals thicker than about 500 Å the loop structures appear, and in the case of crystal having a thickness of 700~1000 Å they are most clearly observed. The loop structures are difficult to observe in the case of the crystals thicker than 1000 Å when 50 kv electrons are used. It may be sure that in the case of very thick crystals ordinarily used, more pronounced changes will occur as suggested in our previous experiments[7] in which replica method was used.

It is very important that micro-mechanism of coagulation of vacancies has been made clear in this experiment in which the effect of electron and x-ray irradiation were carefully examined in alkali halide crystal by many kinds of experimental method.

References

1 For example, P. B. Hirsch *et al*: Phil. Mag. **1** (1956) 677; Phil. Mag. **4** (1959) 721.
2 T. Hibi and K. Yada: J. Electronmicroscopy **9** (1960) 101.
3 T. Hibi and Y. Kawamata: To be published.
4 G. Möllenstedt, K. Graff and R. Speidel: Z. Physik. **167** (1962) 367.
5 G. Möllenstedt: Optik **10** (1953) 72.
6 D. W. Pashley and A. E. B. Presland: Disc. Faraday Soc. **31** (1961) 68.
7 T. Hibi and K. Ishikawa: J. Phys. Soc. Japan **13** (1958) 709; T. Hibi and K. Yada: J. Phys. Soc. Japan **14** (1959) 455.

DISCUSSION

Smoluchowski, R.: First, I should like to congratulate you on the beautiful photographs. Is the instantaneous density of vacancies created during irradiation big enough to create a dynamic equilibrium between small and large cavities?

Yada, K.: Under intense electron irradiation, small cubic cavities change abruptly to large cubic cavities, showing net-like pattern again. It should be noted that in this experiment large cubic cavities are created only in the case of the specimen made from its water solution. It may be considered that diffusion of vacancies becomes easy in the existence of OH^- ions.

Johnston, W. G.: Has it been possible to estimate the temperature of the specimen during the light and heavy irradiation?

Yada, K.: The specimen we used was thermally insulated so that the temperature of the specimen gradually increased during irradiation. At present, we can not estimate accurate temperature during irradiation.