References

1 W. Pitsch: J. Inst. Metals **87** (1958–59) 444; Arch. f. Eisenhüttenwesen **8** (1959) 503.
2 Z. Nishiyama and K. Shimizu: J. Phys. Soc. Japan **15** (1960) 1963. Z. Nishiyama, K. Shimizu, M. Oka and T. Hiromoto: Mem. Inst. Sci. and Ind. Res., Osaka Univ. **16** (1959) 73.
3 P. M. Kelley and J. Nutting: Proc. Roy. Soc. **A259** (1960) 45.
4 W. H. Hall: Proc. Phys. Soc. **A62** (1949) 744.
5 M. Kuriyama: J. Phys. Soc. Japan **15** (1960) 1426.
6 B. E. Warren: *Progress in Metal Physics* **8** (1959) Pergamon Press (London).
7 C. G. Darwin: Phil. Mag. **43** (1922) 800; S. Miyake: *Diffraction of X-rays* (1949), Asakura Shoten (Tokyo), (in Japanese).

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Direct Observation of Crystal Imperfections in KCl Single Crystals by Electronmicroscope

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The processes of change of thin KCl single crystal due to electron irradiation were studied by means of electronmicroscope and electron diffraction. As the result, it was found that by weak irradiation loop structures first appeared and then disappeared showing a lot of small bright specks over the whole crystal. At this stage each diffraction spot had the streaks along ⟨100⟩ directions. By intense irradiation bright squares appeared immediately without showing loop structures. At this stage the diffraction pattern was perfect N-pattern. By using replica technique, it was confirmed that loop structures and large squares were not due to surface structures. By using dark-field method, it was found that the loop structures and bright squares were caused by Bragg reflection. Thus it was proved that the loop structures and bright squares correspond to voids and cubic cavities in the crystal, respectively.

Mechanism of coagulation of vacancies in KCl with electron irradiation was discussed in detail.

1. Introduction

Direct observations of the rolled metallic foil thinned by chemical or electrolytic etching were made electronmicroscopically by Hirsch and others[1]. Jones and Mitchell[2] and Amelinckx and others[3] observed the decorated dislocations in the silver halide and additively coloured alkali halide under light microscope. Hibi and Ishikawa[4] and Hibi and Tomiki[5] made electronmicroscopic observations of coloured alkali halide crystals by using replica technique. Later, the present authors[6] also succeeded in verifying the process of crystallite growth due to X-ray irradiation and crystallite disappearance due to natural bleaching, by using successive replica technique on the definite position of KCl single crystal. It seems to be of much significance to observe directly such changes by using such a thin alkali halide crystal, which makes the use of replica unnecessary. From this point of view, crystal imperfections in KCl single crystal prepared from its water solution were directly observed by means of electronmicroscope and electron diffraction.

2. Experimental method

Thin KCl single crystal obtained by the vacuum drying method already reported[7] was used in this experiment. Successive observations were made under HS-6 electron microscope operating at 50 KV soon after the preparation of the specimen. The electron diffraction pattern of the selected area and the dark-field image were also obtained with the same instrument. Replica technique was often used in examining the surface structure of the specimen. Usual Cr-shadowed carbon replica was tried, and also SiO one-step replica was prepared by evaporating SiO in the specimen chamber of electron microscope without taking out the specimen to the air.

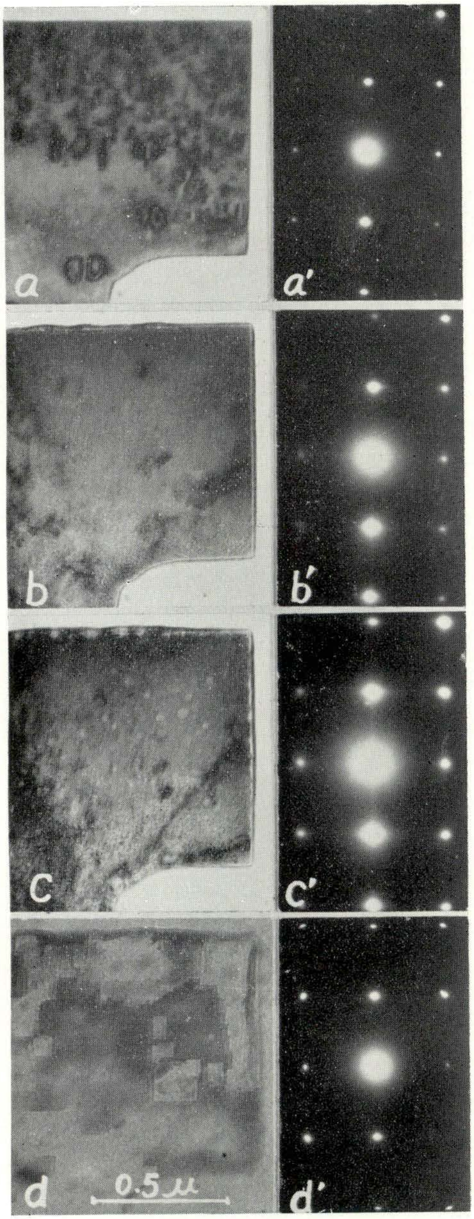

Fig. 1. Successive change of KCl crystal due to electron irradiation.

3. Experimental result

The behaviour of the change in KCl single crystal by electron irradiation depends on the electron beam intensity. A typical example of the process of change caused by weak and intense electron bombardments is shown in Fig. 1. With weak electron irradiations, pair-loops appeared as shown in (a) and developed in the crystal showing perfect N-pattern as shown in (a'). At a certain stage of electron irradiation, their development ceased and then loops began to disappear as shown in (b), when streaks appeared through electron diffraction spots as shown in (b'). A lot of small bright specks then appeared over the whole crystal as shown in (c) and the streaks through its electron diffraction spots became pronounced as shown in (c'). At this stage the crystal gradually changed to polycrystal through continuance of weak electron irradiation, while with intense electron irradiation the bright specks changed to large squares, as shown in (d) showing perfect N-pattern (d'). Fig. 2 shows the detailed change on appearance and disappearance of pair-loops. On the other hand, by the treatment with intense electron irradiation from the beginning, the large bright squares appeared directly without the process showing loop structures. It was confirmed from the experimental result of temperature change in the crystal that with weak electron irradiation stresses concentrated first over the crystal and then annealing effect appeared due to the temperature rise in the crystal. It was also found from the enlarged electron image that the form of the small bright specks was cube. It was also confirmed from

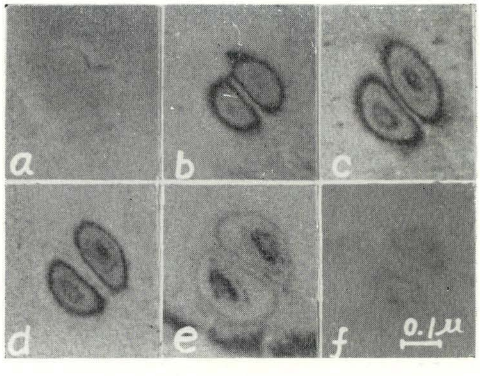

Fig. 2. Successive change of appearance and disappearance of pair-loops.

the electron diffraction examination that the large bright squares and their surrounding part consisted of the same single crystals as shown in Fig. 3.

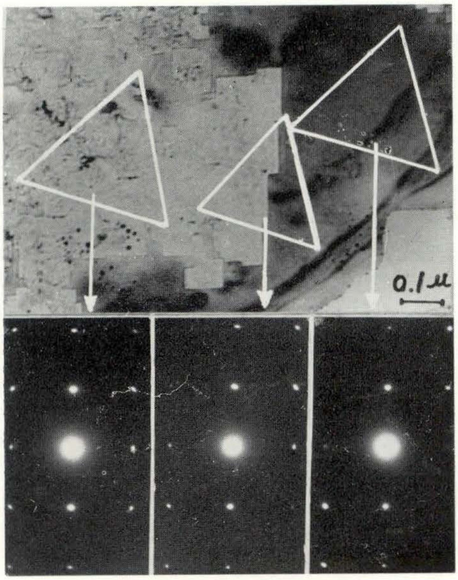

Fig. 3. Electron image of KCl crystal irradiated with intense electron beam and electron diffraction patterns of the selected areas.

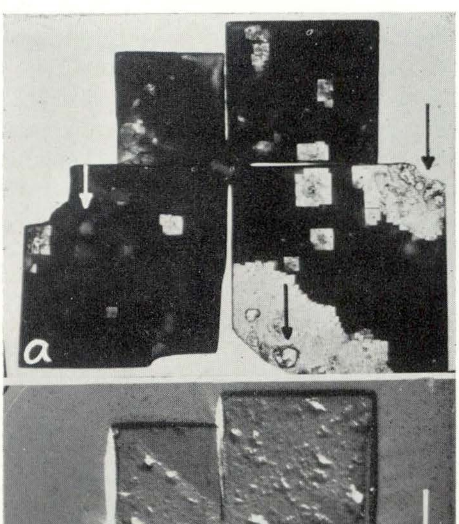

Fig. 4. Electron image and its replica of KCl crystal after intense electron irradiation.

By using replica technique it was examined whether loop structures and large squares appeared on the crystal or not. Fig. 4 (a) shows the electron image of the crystal soon after intense electron bombardment and (b) is its replica obtained without taking the specimen to the air. By comparing (a) with (b), similarities are seen on the structures indicated by the arrows, while no similarity is observable between bright squares and the surface structures. Therefore, this result indicates that these bright squares and also loop structure (though the result on loop structure is omitted here) appeared not on the surface but in the crystal.

To make clear the origin of the loop structure, dark-field electron image method was used. As the result, it was found that the contrast of the loop structure was due to Bragg reflection as shown in Fig. 5. In this figure, direction of loop structure of {200} reflection (c) is different from one of {220} reflection (d).

Therefore, it was considered that by weak electron irradiation there appeared in KCl single crystal the same kind of crystal defects considered by Möllenstedt[8] and Rang[9] to be the voids in mica or lead iodide. It was found that the large bright squares showed

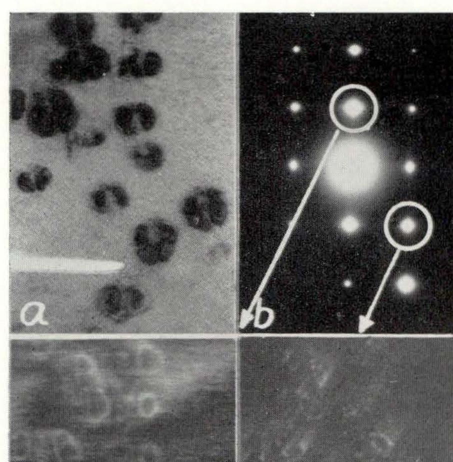

Fig. 5. Bright-field and dark-field images of loop structures.

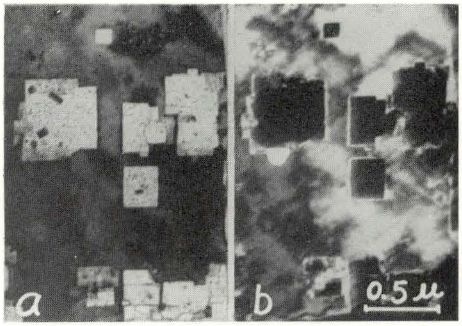

Fig. 6. Bright-field and dark-field images of large bright squares.

also Bragg reflection at an appropriate incident angle of the electron beam as shown in Fig. 6. Same result was obtained on the small bright specks though it is omitted here. Therefore, it was confirmed that these parts were cubic cavities consisting of vacancies.

4. Consideration

It was conceivable from the above-mentioned result that the change in KCl single crystal with electron irradiation is attributed to the following mechanism. By weak electron irradiation, voids consisting of vacancies (10 Å$\sim$100 Å in height and max. 2500 Å in diameter) first appeared in the crystal and developed. Their development ceased after a short time and contraction began. Vacancies escaped from the voids and very small cubic cavities (about 40Å in length in one side) were created here and there along $\langle 100\rangle$ direction of the KCl crystal. By continuing further weak electron irradiation, the small cavities increased in number and finally the diffraction pattern changed to a N-pattern with Debye-rings, indicating the formation of polycrystal having grain boundaries. On the other hand, if an intense electron irradiation is given at this stage, small cubic cavities aggregate with one another forming large cavities and the diffraction pattern changes to the perfect N-pattern as was observed before the irradiation. It may be very important that micromechanism of coagulation of vacancies in ionic crystal has been made clear through the present experiment in which electron microscope and electron diffraction were used.

References

1 P. B. Hirsch *et al.*: Phil. Mag. **1** (1956) 677. Phil. Mag. **4** (1959) 721.
2 D. A. Jones and J. Mitchell: Phil. Mag. **3** (1958) 1.
3 S. Amelinckx *et al.*: Phil. Mag. **2** (1957) 355.
4 T. Hibi and K. Ishikawa: J. Phys. Soc. Japan **13** (1958) 709.
5 T. Hibi and T. Tomiki: J. Phys. Soc. Japan **14** (1959) 445.
6 T. Hibi and K. Yada: J. Phys. Soc. Japan **14** (1959) 455.
7 T. Hibi and K. Yada: J. Electronmicroscopy **9** (1960) 101.
8 G. Möllenstedt: Optik **10** (1953) 72.
9 O. Rang: Optik **10** (1953) 90.

DISCUSSION

N. Kitamura: May I ask what do you think about the origin of streaks in diffraction patterns? We also observed similar streaks in Honjo's laboratory.

K. Yada: Streaks in the diffraction pattern begin to appear when loop structures begin to disappear and when a lot of very small cubic cavities appear the streaks are very pronounced. The least detectable size of the cavities in our case is about 40Å in length in one side, but actually smaller cavities may exist in the interior of the crystal. We think that the origin of the streaks is attributed to these very small cavities arranging along $\langle 100\rangle$ directions.

G. Honjo: I think that Dr. Yada's interpretation is right so far as the streaks which he has observed are concerned. It seems to me that Dr. Yada's streaks are of origin different from those observed in my laboratory.

K. Yada: In this paper we reported only the result of the specimens having $\{100\}$ base plane, which showed the streaks along $\langle 100\rangle$ directions in the diffraction pattern. In the case of the specimen having $\{111\}$ or $\{211\}$ base plane we observed the network of streaks in which each component of the network corresponded to the $\langle 100\rangle$ directions of the reciprocal lattice. So, we think that streaks are due to very small cubic cavities.

E. SUITO: I think that the cubic cavities were produced by the evaporation of the material due to the electron bombardment. How do you think the relation between the small cavities and the cubic cavities?

K. YADA: In previous experiments we observed successively the growth of crystallites on the cleavage surface of alkali halide with X-ray irradiation, and also in the present experiment we observed the volume expansion of KCl with electron irradiation. These results suggest that small cubic cavities resulted from the aggregation of those vacancies in the crystal which are newly created with X-ray or electron irradiation as well as those inherently existing in the crystal.

Though the evaporation of the material may occur to some extent in the case of intense electron irradiation, we do not think that the cubic cavities are produced by evaporation. We think that the large cavities are formed as the result of aggregation of the small cubic cavities with intense irradiation.

N. KATO: In your cases, do the loop pairs move or not?

K. YADA: In our case the size of the pair loops gradually changed with electron irradiation, but the position of the loop did not move.

P.B. HIRSCH: It should be mentioned that Dr. Pashley has shown that ion bombardment takes place sometimes in the electron microscope, the ions presumably being produced in the gun. These ions cause defects to be produced in gold foils, and they would have made similar observations in Zn, Mg, and Cd (Price, Lally; unpublished). Dislocation loops are formed in this way.

In experiments in which the production of damage is observed in the microscope, the possibility of ion damage as well as electron damage should be born in mind.

K. MIHAMA: In the course of our experiments on ion bombardment, partly carried out in CNRS at Bellevue in France, we observed the similar image characterized by a pair of circles like Rang's image for the specimen bombarded by an ion beam. The width of such a pair of circles varied under the electron bombardment during the observation by the electron microscope, but the position did not change. Furthermore, the intensity difference between each circles of the pair was observed frequently and this difference also varied sensitively by the electron bombardment in the microscope.