The atoms C_4, C_5, C_6, N and O_2 are again coplanar; this plane makes an angle of 6° with the first. Finally, the planar acetyl group, i.e. the atoms C_7, C_8, O_2, O_3 and N, is rotated 7° upward about the bond N–O_2.

The deviations from planarity are less systematic in the case of β-ClBOA, as can be seen from the x-parameters in Table 3. The acetyl group $O_2C_7C_8O_3$ is rotated around the bond O_2–C_7 out of the 'plane' of the rest of the molecule, so that the distance between the non-bonded atoms O_3 and N is slightly increased.

The authors wish to thank Prof. Dr E. Havinga for his stimulating interest, Prof. Dr H. Wynberg for reading the manuscript and Mr A. Kreuger for his achievements in the low-temperature diffraction experiments. The X-ray apparatus was put at our disposal by the Netherlands Organization for Pure Research, Z.W.O.

References

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698.
FISCHMANN, E., MACGILLAVRY, C. H. & ROMERS, C. (1961). *Acta Cryst.* **14**, 753.
KEHRMANN, F. (1894). *Ann.* **279**, 27.
ROMERS, C. & FISCHMANN, E. (1960). *Acta Cryst.* **13**, 808.
TROTTER, J. (1960). *Acta Cryst.* **13**, 95.
UMANS, A. J. H. (1959). Thesis, University of Leiden.

Acta Cryst. (1961). **14**, 763

Reduction of U_3O_8 to U_3O_{8-x} in Mode of Crystallographic Out-of-Step

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When a single crystal of orthorhombic U_3O_8 is heated *in vacuo*, its electron diffraction patterns exhibit an interesting sequence of changes. First, some of the diffraction spots suffer a splitting, and then the splitting becomes pronounced with the elevation of temperature. The reduction of U_3O_8 to U_3O_{8-x} underlying these pattern changes seems to proceed, until the lower composition limit of U_3O_8 phase in the UO_2–U_3O_8 phase diagram is reached. An interpretation for these anomalous diffraction patterns is carried out on the basis of diffraction theory of out-of-step structure. The physical quantities involved in the interference function, made up for the present purpose, are determined by comparing implications of the resulting interference function with the patterns actually obtained. By this, the mode of out-of-step in this problem is revealed, together with its physical meaning. It is concluded that a particular manner of valency conversions of uranium ions takes place in the reduction of U_3O_8 to U_3O_{8-x}, and that slight positional changes accompanying the valency conversions are responsible for the pattern changes.

In the course of the study of calcination of precipitated ammonium diuranate ($(NH_4)_2U_2O_7.xH_2O$) to U_3O_8, an extremely unusual crystal growth has been encountered (Doi *et al.*, 1960). Under particular conditions of the precipitation and the subsequent calcination, the resulting U_3O_8 particles take a characteristic shape, so thin as to be semitransparent to electron beams, and have, moreover, an almost single-crystalline atomic arrangement. Such a situation will be favourable in utilizing the present-day electron optical techniques. For example, crystallographic aspects in a variety of chemical changes of U_3O_8 will be successfully investigated, since changes in morphology and atomic arrangement can be observed both *in situ* in an advanced electron microscope. As the first step, the study of U_3O_8 heated *in vacuo* is dealt with in the following.

Experimental

U_3O_8 was prepared by calcination at 600 to 700 °C. of ammonium diuranate precipitated under a particular condition (Doi *et al.*, 1960). The powder was mounted on a carbon-backed collodion film. The U_3O_8 particles meeting the purpose were chosen by observing on the fluorescent screen their electron microscopic images along with their selected area electron diffraction patterns. The heating of the specimen was carried out *in situ* in the apparatus by intensifying the electron beam impinging on it. Although the exact temperature of the specimen at varied stages was unknown, the maximum temperature attained seemed to be about 400 °C. The electron microscope used was of JEM-5Y-type of Japan Electron Optics Laboratory. An accelerating voltage for electrons of 80 kV. was usually used.

Results

The electron micrograph of a typical U_3O_8 particle is shown in Fig. 1. Since the particle size of the ammonium diuranate used is of the order of $0{\cdot}1\mu$, the crystal growth of U_3O_8 during the calcination is evidently very particular (Doi *et al.*, 1960). The particle is very thin in the direction of the electron beam, its lateral dimension is as large as several microns, its periphery takes a characteristic shape, and it involves many holes of a characteristic shape. Moreover, the corresponding electron diffraction pattern (Fig. 2) shows that the particle is almost a single crystal. The analysis of the pattern (Uchikoshi *et al.*, 1960) shows that all the diffraction spots are compatible with the crystal structure of orthorhombic U_3O_8 proposed by Andresen (1958) or Chodura & Malý (1958). It shows further that the crystal is thin along *c*-axis, and that the crystal involves twins, which

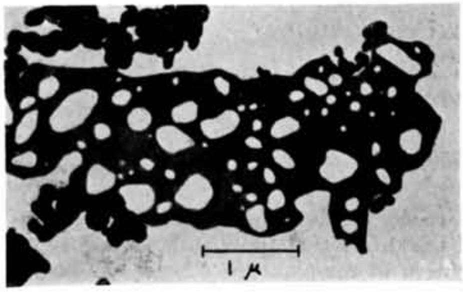

Fig. 1. Electron micrograph of a typical U_3O_8 particle.

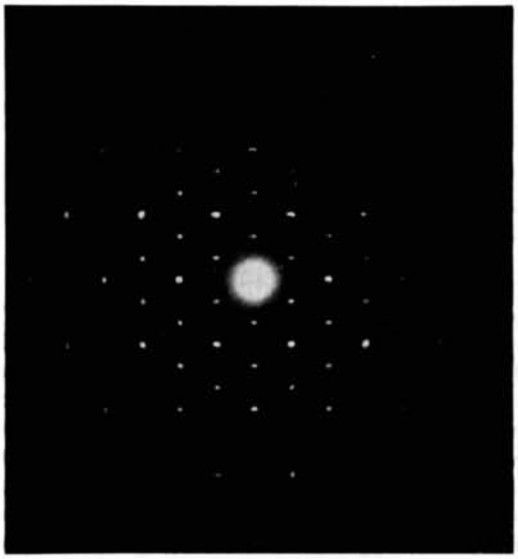

Fig. 2. Electron diffraction pattern of the specimen of Fig. 1.

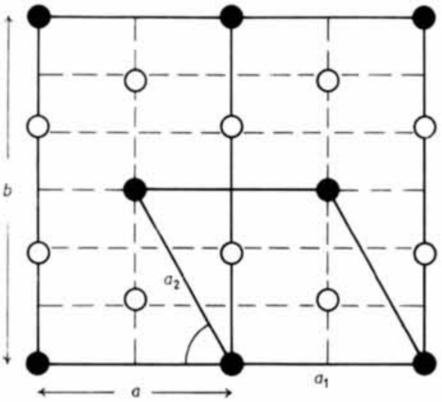

Fig. 3. Positions of U^{6+} (full circles) and U^{5+} (open circles) of orthorhombic U_3O_8 on (001), according to Andresen (1958). $a=6{\cdot}704$, $b=11{\cdot}95$, $c=4{\cdot}142$ Å. The broken lines bisect a, and divide b into six equal parts. Parameters of U^{6+} are $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, 0$, and those of U^{5+} are $0, \pm y, 0$; $\frac{1}{2}, \frac{1}{2}\pm y, 0$, where $y=0{\cdot}315$. a_2 is calculated to be $6{\cdot}851$ Å. The acute angle between a and a_2 is calculated to be $60{\cdot}7°$.

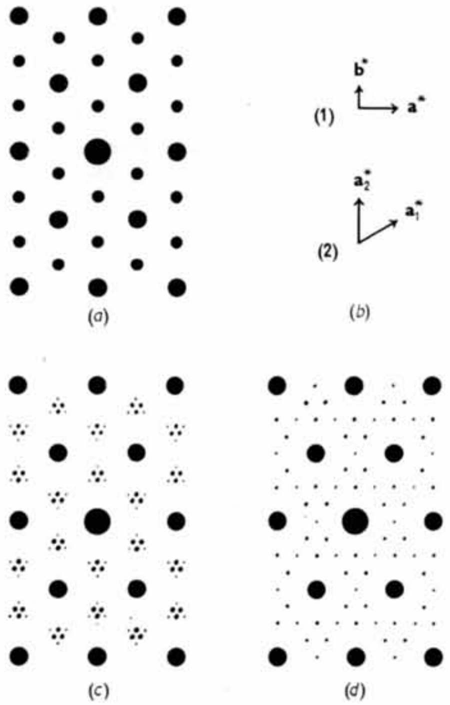

Fig. 4. Schematic depictions of the diffraction patterns of Figs. 2 and 5–8. The largest circles indicate the undeviated beams. The representation of the spot intensities by the circle areas is only schematic. (*a*) corresponds to Fig. 2. The spots in (*a*) are readily indexed with the aid of the reciprocal-lattice unit vectors in (*b*). The vectors in (*b*,1) and (*b*,2) are derived, respectively, from the direct-lattice unit cells of *ab* and a_1a_2 in Fig. 3. (*c*) corresponds to Figs. 5–7, the grade of spot splittings being depicted for convenience so as to correspond to $M=3$ (regarding M, see text). (*d*) corresponds to Fig. 8, the spots due to UO_2 being omitted. In all depictions the complexity arising from the deviation of the crystal from being hexagonal and the spot elongations are both neglected.

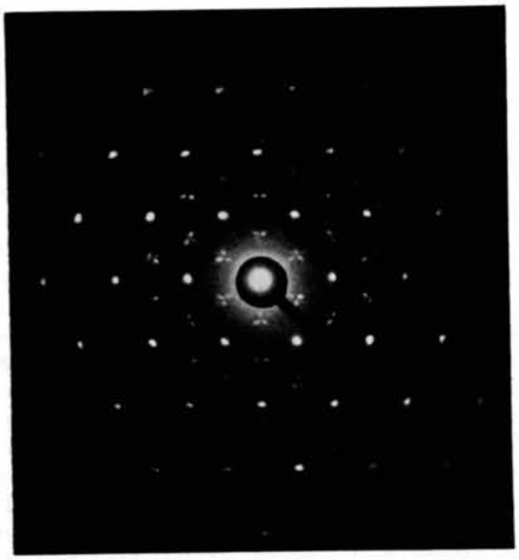

Fig. 5.

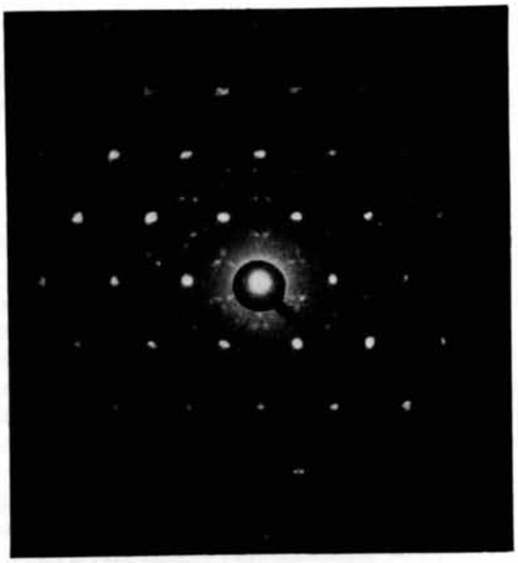

Fig. 6.

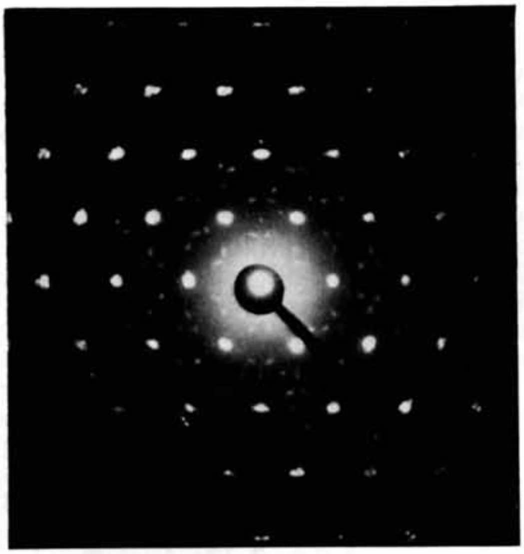

Fig. 7.

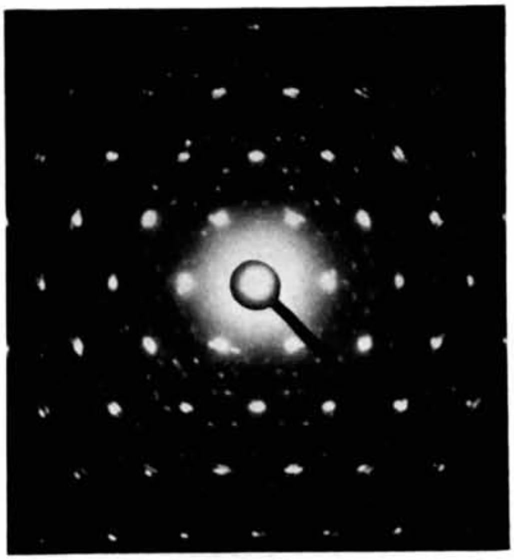

Fig. 8.

Figs. 5–8. Electron diffraction patterns obtained by successive heatings of the specimen of Figs. 1 and 2. A minor part of the spots of Fig. 8 are due to UO_2, to which U_3O_8 is eventually reduced.

mutually make about 60° around *c*-axis. Such a twinning is well expected, since the crystal is regarded as pseudohexagonal (see below).

The arrangement of uranium ions on (001) according to neutron diffraction data by Andresen (1958) (orthorhombic, space group D_2^6–$C222$, two molecules in a unit cell) is depicted in Fig. 3. The oxygen ions are omitted there because of their inefficiency in scattering electrons as compared with uranium ions. It is to be noted that uranium ions are all arranged on (001) in a nearly hexagonal manner, and that there are one U^{6+} ion and two U^{5+} ions per molecule. Although this model of Andresen differs slightly from that of Chodura & Malý (1958), it is sufficient to refer only to the former for the present purpose.

The pattern of Fig. 2 is illustrated in a much simplified manner in Fig. 4(*a*), whose spots are readily indexed with the aid of Fig. 4(*b*). Regarding the different choices of unit cell, see Fig. 3.

Now, by being heated *in vacuo* the U_3O_8 pattern (Fig. 2) undergoes very interesting changes shown in Figs. 5–8. First, the comparatively weaker spots of Fig. 2 split into groups of spots elongated along the splitting direction (Fig. 5). The symmetry of the resulting spot group around its centre is approximately trigonal. The sense of these trigonal groups is not of one kind, but of two kinds, depending on the indices of the lost spot at the centre. A pair of spots along a splitting direction are not symmetric with respect to the lost spot. The distance of the farther and weaker one from the lost spot is twice that of the nearer and stronger one. The split becomes more pronounced with the elevation of temperature (Figs. 6 and 7), and reaches eventually a final stage (Fig. 8). The temperature corresponding to Fig. 8 is presumably about 400 °C. At the final stage the anomalous spots, which now suffer a maximum split, are again sharp though weak. Throughout this sequence of changes the comparatively stronger spots of Fig. 2 remain almost unchanged. This implies that a certain elemental feature of the structure is conserved throughout the changes. The outline of the pattern changes is illustrated in the much simplified depictions of Fig. 4. The electron micrograph corresponding to Fig. 8 is shown in Fig. 9. As compared with Fig. 1, this shows no severe changes in particle shape, although tiny cracks and a change in extinction contours are observed.

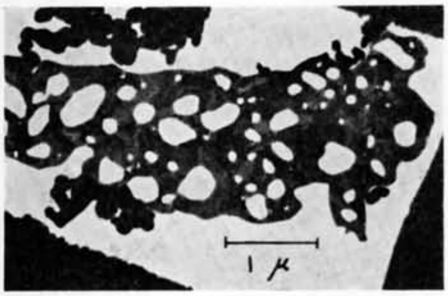

Fig. 9. Electron micrograph of the specimen of Fig. 8.

According to Uchikosi *et al.* (1960), a minor part of the spots of Fig. 8 are due to uranium dioxide (fluorite-type cubic, $a=5{\cdot}47$ Å) in a special orientation, and by being heated further the crystal becomes entirely reduced to uranium dioxide. It follows from this that what occurs under the present experimental condition is reduction of U_3O_8 towards UO_2. The above pattern changes suggest that before conversion of the orthorhombic lattice of U_3O_8 to the cubic lattice of UO_2 the former undergoes a modification. The chemical formula for the modified stages should be U_3O_{8-x}, where x is a small positive variable.

In Andresen's model for U_3O_8 (Fig. 3) the deviation from being hexagonal is reflected in the deviation of the acute angle between a and a_2 from 60°. In Figs. 2 and 5–8 the angle in question may be calculated from the slight radial separation of a strong spot, which stands sufficiently far from the undeviated spot. It amounts to 60·7° for Fig. 2, in accord with Andresen's model, and to 61·0° for Fig. 8. This implies that the deviation becomes more pronounced as the reduction proceeds. That the stronger spots, which suffer no splitting on heating, become somewhat diffuse with the reduction is ascribed to this situation, and, in addition, to the cracking of the crystal mentioned above.

Preparative to interpretation of results

It will be evident that the anomalous patterns of Figs. 5–8 are due to a certain kind of imperfect crystal, and that the imperfection becomes more pronounced as the reduction proceeds. The proper approach to interpretation of these patterns seems to lie in adoption of the theory regarding out-of-step structure. In a crystal having this structure a relative shift between adjacent domains occurs periodically, in each domain atomic positions being regular, so that for interference phenomena there is a definite phase difference between them. Many contributions to this field are reviewed, for example, in a report by Ogawa & Watanabe (1954) and in monographs by Raether (1957) and by Ogawa (1958). Lately the theory became more refined (Perio & Tournarie, 1959*a*; Okuzumi *et al.*, 1959; Perio & Tournarie, 1959*b*). Moreover, owing to the advanced electron optical techniques, spacings of about 20 Å or less of periodic out-of-steps became possible to be directly resolved (Ogawa *et al.*, 1958; Ogawa *et al.*, 1959; Glossop & Pashley, 1959).

The present problem seems, however, to be different from those studied hitherto in the following points. (1) The substances investigated hitherto are almost confined to ordered binary alloys, whose axes are mutually perpendicular (mostly tetragonal). On the contrary, the orthorhombic lattice of the uranium ions in U_3O_8 is regarded as pseudohexagonal (Fig. 3). (2) With the binary alloys the anomaly occurs only at superlattice reflexions, apart from weaker satellites around the undeviated and normal spots, pointed out first by Ogawa & Watanabe (1954). For U_3O_8 the term 'superlattice' cannot be applied in its proper meaning, although the arrangement of U^{6+} and U^{5+} on (001) (Fig. 3) has an aspect of superlattice. A noticeable situation in this case is that the spots to be split on heating are such that their intensities are sensitive to the positional deviation of U^{5+} from $(0, \pm\frac{1}{3}, 0)$ or $(\frac{1}{2}, \pm\frac{1}{6}, 0)$. (3) For the ordered binary alloys it is expected almost *a priori* that the relative shift between adjacent domains by half the face diagonal of the *elemental* unit cell plays a principal role in giving rise to anomalous diffraction pattern. Such domains deserve the term 'anti-phase', which is being used widely. On the contrary, for the present problem no *a priori* expectations are available regarding the mode of its out-of-step. (4) However, the present problem has a situation favourable for analysis. If the relative shift between adjacent domains is represented by a vector, it lies most likely on (001), perpendicular to the electron beam used for inspection. This is supported by the structure of U_3O_8 (Fig. 3). For the binary alloys this is generally not the case.

For the boundary planes between out-of-step domains the following three crystallographic planes may be possible; (010), (110), and ($\bar{1}$10), expressed in the orthorhombic system. Although the three are similar with respect to the arrangement of U^{6+} and U^{5+}, only the last two are crystallographically equivalent to each other. Examination of Figs. 5–8 shows that at a given small portion of the crystal the boundary planes consist of only one of the three crystallographic planes. If these two crystallographic planes coexist as boundaries, a spot anomaly more complex than in Figs. 5–8 will result, owing to double split of diffraction spots (Ogawa *et al.*, 1955; Watanabe & Ogawa, 1956; Hirabayashi & Ogawa, 1957; Watanabe, 1958; Perio & Tournarie, 1959*a*; Okuzumi *et al.*, 1959). On the same account, coexistence of three kinds of crystallographic planes as domain boundaries is also excluded.

Taking into account various uranium-to-oxygen distances in the model of Andresen (1958), (010) seems to become domain boundaries prior to the other two. In the following, therefore, (010) will be chosen as boundaries. The other two choices are expected not to modify essentially the following interpretation. The treatment on the basis of one kind of domain boundary is concerned with split along only one direction, perpendicular to the boundary. However, by introducing to the results a triad operation around *c*-axis, corresponding to the presence of 60° twinning in the crystal, all the spots of Figs. 5–8 are expected to be accounted for.

Since the orthorhombic unit cell contains two U_3O_8 molecules (Fig. 3), replacement of it by a pseudohexagonal unit cell containing only one molecule seems to be preferable for analyzing the patterns. As such a unit cell a_1a_2c shown in Fig. 3, whose $a_1(=a)$ is parallel to the domain boundaries, will be chosen. In Fig. 4(*b*) the reciprocal-lattice unit vectors, $\mathbf{a}^*\mathbf{b}^*$ and $\mathbf{a}_1^*\mathbf{a}_2^*$, corresponding respectively to the orthorhombic and pseudohexagonal lattices, are shown. If hkl and h_1h_2l denote respectively the indices of a crystallographic plane in terms of both lattices, the transformation equations are

$$\begin{cases} h_1=h \\ h_2=\frac{1}{2}(k-l) \end{cases} \qquad \begin{cases} h=h_1 \\ k=h_1+2h_2 \, . \end{cases}$$

In addition, it will be assumed, according to the consideration mentioned before, that the phenomena underlying the anomalous patterns take place only two-dimensionally.

Now, what is first to be done is to make up the interference function so as to meet the present problem. Then, by comparing the spot splittings derived from the resulting interference function with the patterns actually observed the out-of-step mode in question will be revealed, together with the structure of U_3O_{8-x} and its change in heating.

Interpretation of results, I

The analytical expression in general of the vector representing an out-of-step in question is

$$\mathbf{P}=p_1\mathbf{a}_1+p_2\mathbf{a}_2 \, ,$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the direct-lattice unit vectors, and p_1 and p_2 constants. Let the number of unit cells along $\mathbf{a}_1$ be L, an out-of-step do occur at every Mth unit cell along $\mathbf{a}_2$, and the number of such out-of-step domains be N. The position of a lattice point is generally represented by the vector:

$$\mathbf{r}_{lmn}=(l+np_1)\mathbf{a}_1+\{m+n(M+p_2)\}\mathbf{a}_2 \, ,$$

where

$$l=0, 1, \ldots, L-1; \quad m=0, 1, \ldots, M-1; \quad n=0, 1, \ldots, N-1 \, .$$

Therefore, the interference function is expressed as

$$\begin{aligned} |G| &= |G_1|\cdot|G_2'|\cdot|G_2''| \\ &= \left|\frac{\sin \pi L A_1}{\sin \pi A_1}\right| \cdot \left|\frac{\sin \pi M A_2}{\sin \pi A_2}\right| \\ &\quad \times \left|\frac{\sin \pi N(MA_2+p_2A_2+p_1A_1)}{\sin \pi(MA_2+p_2A_2+p_1A_1)}\right| \, , \end{aligned}$$

where A_1 and A_2 are continuous variables in the reciprocal space.

Since $|G_1|$ and $|G_2'|$ have the ordinary form of interference function, their meaning is readily understood. The spot splittings along $\mathbf{a}_2^*$, only with which we are now concerned, must be accounted for by the product $|G_2'|\cdot|G_2''|$, where principal maxima of $|G_2'|$ occur with the period of unity (taking $|\mathbf{a}_2^*|$ as the unit), and those of $|G_2''|$ with a much smaller period. (Although $|G_2''|$ involves not only A_2 but also A_1, this does not change positions of high values of $|G_1'|\cdot|G_2''|$, as will be understood below.) In view of the general theory regarding spot anomalies due to out-of-step structure (Raether, 1957; Ogawa, 1958), it is here simply assumed, to the first approximation, that a pair of split spots appear *at* two principal maxima of $|G_2''|$, which fall on the bell-shaped curve involving a principal maximum of $|G_2'|$, whose width is $2/M$. It is to be noted that generally the two are arranged asymmetrically with respect to the principal maximum of $|G_2'|$, which is now extinguished.

Since L may be assumed as large, A_1 and A_2 for the split spots are written $A_1=h_1$ and $A_2=h_2+\Delta h_2$, where Δh_2 represents the splitting under consideration. Therefore, the expression in the parenthethes in $|G_2''|$ becomes

$$\begin{aligned} &MA_2+p_2A_2+p_1A_1 \\ &=Mh_2+(M+p_2)\Delta h_2+p_2h_2+p_1h_1 \, . \end{aligned}$$

Examination of Fig. 4(*c*) shows that the splitting manner depends on the value of h_2-h_1. This implies that the last two terms of the above expression must take the form $C(h_2-h_1)$, where C is a constant. This leads to $p_1=-p_2$. Moreover, combination of Fig. 4(*c*) and Fig. 4(*b*, 2) shows that the arrangement of all the spots along $\mathbf{a}_2^*$ has a period of $3|\mathbf{a}_2^*|$. This implies $p_2=t/3$, where t is an integral constant not divisible by three, so that $p_2=-p_1=t/3$. Thus we obtain

$$|G_2''| = \left| \frac{\sin \pi N\{Mh_2 + (M+t/3)\Delta h_2 + t/3(h_2-h_1)\}}{\sin \pi\{Mh_2 + (M+t/3)\Delta h_2 + t/3(h_2-h_1)\}} \right| .$$

Principal maxima of $|G_2''|$ occur, when the expression in the braces becomes equal to zero or an integer. Since Mh_2 is invariably zero or an integer, this is equivalent to

$$(M+t/3)\Delta h_2 + t/3(h_2-h_1) = u ,$$

where u is zero or an integer. Fig. 4(*c*) suggests that when h_2-h_1 is divisible by three, i.e. $h_2-h_1=3i$, where i is zero or an integer, $\Delta h_2=0$. For this case, therefore, $u=it$. For the cases of $h_2-h_1=3i\pm1$, the u values are generally different from it; i.e. $u=it+v$, where v is zero or an integer. On the other hand, t is an integral constant not divisible by three; i.e. $t=3j\pm1$, where j is zero or an integer. Using these u and t, the Δh_2 values are calculated from the above formula:

$$\left\{ \begin{aligned} & h_2-h_1=3i+1: \\ & \qquad \Delta h_2 = (3v-t)/(3M+t) = (3(v-j)\mp1)/(3M+t) \\ & h_2-h_1=3i-1: \\ & \qquad \Delta h_2 = (3v+t)/(3M+t) = (3(v+j)\pm1)/(3M+t) . \end{aligned} \right.$$

Since it is sufficient to take into account only the smallest possible value of $|\Delta h_2|$ on the plus and minus sides, the possible values of $|\Delta h_2|$ are confined to $1/(3M+t)$ and $2/(3M+t)$.

Close examination of the above expressions for Δh_2 leads to the following two possibilities for relations between $(\Delta h_2)_+$ and $(\Delta h_2)_-$, the plus and minus values of Δh_2, respectively:

$$(1):\ t=3j+1: \left\{ \begin{aligned} & h_2-h_1=3i+1: & (\Delta h_2)_+ &= -2(\Delta h_2)_- \\ & h_2-h_1=3i-1: & 2(\Delta h_2)_+ &= -(\Delta h_2)_- \end{aligned} \right.$$

$$(2):\ t=3j-1: \left\{ \begin{aligned} & h_2-h_1=3i+1: & 2(\Delta h_2)_+ &= -(\Delta h_2)_- \\ & h_2-h_1=3i-1: & (\Delta h_2)_+ &= -2(\Delta h_2)_- . \end{aligned} \right.$$

Figs. 5–8 show that the former is our case, the latter being never encountered. Thus, the Δh_2 values measurable in the diffraction patterns are concluded to be expressed as

$$\left\{ \begin{aligned} & h_2-h_1=3i: \\ & \qquad \Delta h_2=0 \\ & h_2-h_1=3i+1: \\ & \quad (\Delta h_2)_+=2/(3M+t),\ (\Delta h_2)_-=-1/(3M+t) \\ & h_2-h_1=3i-1: \\ & \quad (\Delta h_2)_+=1/(3M+t),\ (\Delta h_2)_-=-2/(3M+t) , \\ & \text{where} \qquad t=3j+1 . \end{aligned} \right.$$

Although M and t are both necessary for knowing the structure of U_3O_{8-x}, x being a variable, they are not determined uniquely in these expressions. This difficulty will be overcome by examining the final stage (Figs. 8 and 4(*d*)). It is seen there that $|\Delta h_2|=\frac{1}{4}$ or $\frac{1}{2}$, so that $3M+t=4$. According to the general property of interference function, M at the final stage must be extremely small, rather equal to unity, since $|\Delta h_2|$ as large as $\frac{1}{4}$ or $\frac{1}{2}$ is actually observed. From $M=1$ it follows that $t=1$. (The structure with $M=1$ is no more an out-of-step structure. Regarding this point, see below.)

It seems natural to suppose that **P** derived from $t=1$, *i.e.*

$$\mathbf{P} = -\mathbf{a}_1/3 + \mathbf{a}_2/3$$

is the unique vector throughout the changes under consideration. The changes of the structure of U_3O_{8-x} with reduction are now understood as a process, where M decreases from a large value down to unity, $t=1$ holding throughout. The U_3O_{8-x} structure for $M=3$, for example, is schematically depicted in Fig. 10. It is seen that with respect to phase there are three kinds of domains. It is to be noted that the *true* unit cell in the *extended* pseudohexagonal system has the lattice constants of a_1 and $(3M+1)a_2$, while the *true* unit cell in the orthorhombic system has those of a and $(3M+1).b/6$ for odd M, and of a and $(3M+1).b/3$ for even M. It is also to be noted that the product MN decreases with increasing density of domain boundary, therefore, as the reduction proceeds. This is in contrast to the cases of ordered binary alloys, where no chemical reactions take place, therefore, MN is kept constant, unless the crystal is broken into incoherent regions.

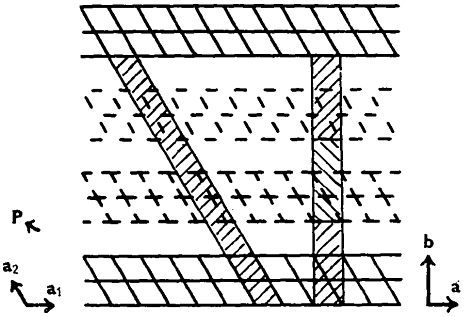

Fig. 10. Arrangement of the *elemental* pseudohexagonal unit cells in U_3O_{8-x} with $M=3$. A *true* unit cell in the *extended* pseudohexagonal system and three *true* orthorhombic unit cells are hatched.

The above expressions for Δh_2 imply that Δh_2, which increases as the reduction proceeds, must take invariably a discrete value, if M has a single value throughout the crystal. Actually, this is not the case, the split spots showing almost invariably an elongation (Figs. 5–7). This implies presumably that the M values fluctuate considerably around a predominant value. According to Fujiwara (1957), if there is a certain mixing of two M values in a crystal, the resulting spots show no elongations, and M deduced from the observed splittings becomes a fraction, not an integer. However, an elongation such as in the present case may be expected, if the M values in the crystal are much more random than in his treatment. The values of M deduced from the splittings actually observed are 1·8 to 5·3 for Fig. 5, 1·1 to 3·7 for Fig. 6, 1·0 to 2·8 for Fig. 7, and 1·0 for Fig. 8.

That the elongation disappears at the final stage (Fig. 8) is well understood, since there the M values tend to a single value of unity. The situation regarding intensities of the split spots that the stronger ones correspond invariably to the smaller $|\Delta h_2|$ is also qualitatively consistent with the interpretation described so far.

Since 60° twinning is presumably unavoidable in U_3O_8 and U_3O_{8-x}, all the normal and anomalous spots of Figs. 5–8 are reasonably accounted for by introducing a triad operation to the above results.

Interpretation of results, II

It has been concluded in the foregoing section that the vector representing the out-of-step in question is $\mathbf{P} = -\mathbf{a}_1/3 + \mathbf{a}_2/3$. This is such that its tail is at the centre of a U^{6+} ion, while its head is very near the centre of a U^{5+} ion, which is the left upper neighbour of the former (Fig. 3). That **P** points to the left upper side is due to the situation that the spot indices have been classified with respect to $h_2 - h_1$. If $h_2 + 2h_1$ is used instead of $h_2 - h_1$, the vector pointing to the right upper side will be obtained. Both treatments are mathematically equivalent, and, moreover, both resulting vectors are crystallographically equivalent to each other. Therefore, generality of the discussion is not lost by taking **P** as above.

The most reasonable physical meaning of the vector **P** seems to be as follows. The head of the vector **P**, whose coordinates are $(-a_1/3, a_2/3)$, becomes newly a lattice point of *elemental* unit cell. Taking into account the oxygen ions surrounding a uranium ion, this implies most likely the conversion of U^{5+} to U^{6+} accompanied by the slight positional change. As to the U^{6+} at the tail of the vector, it is presumably reduced to U^{5+} or U^{4+}, also accompanied by a slight positional change of an unknown amount (see below). From this interpretation of **P** it follows that the density of U^{6+} in the crystal decreases with increasing density of domain boundary, therefore, with decreasing M. Thus, this interpretation is in harmony with the actual chemical change that the crystal is being successively reduced, i.e. oxygen ions are being removed. The reason why **P** points outwards (i.e. t or $p_2 > 0$), not inwards, is now understood. That t amounts to 1 (i.e. $p_1 = -\frac{1}{3}$ and $p_2 = \frac{1}{3}$), not to 2, implies presumably that the crystal is reluctantly reduced.

The interference function, $|G| = |G_1| . |G_2'| . |G_2''|$, discussed in the foregoing section is concerned with the two-dimensional arrangement of *elemental* unit cells, each consisting of one U^{6+} ion and two U^{5+} ions. Since the coordinates of these three are 0, 0; ya_1, $2ya_2$; $(1-y)a_1$, $(1-2y)a_2$, respectively, where $y = 0{\cdot}315$ (Fig. 3), the structure factor F of the *elemental* unit cell is given by

$$F = 1 + \exp 2\pi i(yA_1 + 2yA_2) + \exp 2\pi i\{(1-y)A_1 + (1-2y)A_2\}\,.$$

Here, and also in the following, the scattering factor of a uranium ion is assumed as unity, regardless of its valency.

On the other hand, according to the above consideration of **P**, three *extra* ions (U^{5+} or U^{4+}) must be introduced into a *true* unit cell expressed in *extended* pseudohexagonal system. They are indicated by crosses in Fig. 11 (see also Fig. 10). Let the part in Fig. 11 bounded by broken lines be a *temporary* unit cell with lattice constants of a_1 and Ma_2. This contains M U^{6+} ions, $2M$ U^{5+} ions, and an *extra* ion. The coordinates of the U^{6+} ions, each being accompanied by two U^{5+} ions, are 0, 0; 0, a_2; ...; 0, $(M-1)a_2$. Those of the *extra* ion are $\varepsilon_1 a_1$, $(M+\varepsilon_2)a_2$, where ε_1 and ε_2 are unknown small constants. Therefore, using A_1 and A_2 same as before, the structure factor F_t of the *temporary* unit cell is given by

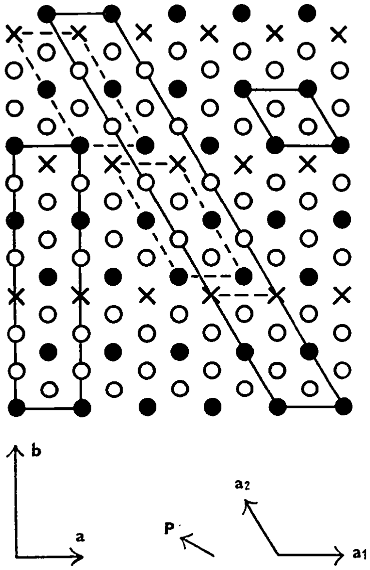

Fig. 11. Arrangement of U^{6+} (full circles), U^{5+} (open circles), and *extra* ions (crosses) on (001) of U_3O_{8-x} with $M = 2$. Open circles and crosses indicate only approximate positions. Solid lines indicate an *elemental* pseudohexagonal unit cell, a *true* unit cell in the *extended* pseudohexagonal system, and a *true* orthorhombic unit cell. Broken lines indicate *temporary* unit cells in the *extended* pseudohexagonal system.

$$F_t = \{1 + \exp 2\pi i A_2 + \ldots + \exp 2\pi i(M-1)A_2\} . F + \exp 2\pi i\{\varepsilon_1 A_1 + (M + \varepsilon_2)A_2\}\,.$$

Now, the structure of U_3O_{8-x} with *any* M-value can be regarded as an out-of-step structure, where an out-of-step occurs at *every temporary* unit cell, the mode of the out-of-step being represented by the vector **P** as before. The consideration in the first part of the foregoing section shows, therefore, that for the interference function G_t regarding the arrangement of *temporary* unit cells M of $|G_2'|$ is unity. Thus the product of the interference function and the absolute value of the structure factor is given by

$$|G_t|.|F_t|=|G_1|.|G_2''|.|F_t|\ ,$$

where $|G_t|=|G_1|.|G_2''|$ determines primarily positions and intensities of reflexions, and $|F_t|$ modifies their intensities.

In F_t the first term arises from $3M$ ions, while the last term from only one *extra* ion. Therefore, the contribution of the latter to F_t is unimportant. If this is neglected, the above formula turns into

$$|G_t|.|F_t|=|G_1|.|G_2'|.|G_2''|.|F|\ ,$$

which is nothing but what was discussed in the foregoing section, apart from the intensity determining factor $|F|$. Thus, it is concluded that the interpretation in the foregoing section is justified qualitatively also for the U_3O_{8-x} structure proposed in this section, and that the anomalous sequence of changes of the diffraction patterns has been reasonably correlated with the out-of-step phenomenon occurring in the reduction process.

Discussion

The present work has thus revealed that the reduction or decomposition of U_3O_8 to U_3O_{8-x} proceeds in a mode of crystallographic out-of-step, although the quantity M involved in the theory is not so definite at each stage of the reduction. The change in line-up of the three kinds of uranium-ion-planes during the reduction is schematically illustrated in Fig. 12. Since the average spacing between adjacent U-planes is ~ 2 Å (Fig. 3), the spacing between adjacent out-of-steps in the crystal under reduction is $\sim 2(3M+1)$ Å. Such spacings are expected to be directly observed by electron microscopy, if they exceed the limit of the resolving power. The study along this line is now under way, and the results will be reported later.

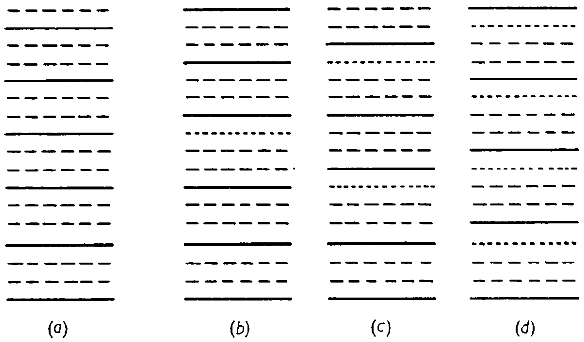

Fig. 12. Successive stages of line-up of U-planes in the reduction of U_3O_8 to U_3O_{8-x}. Solid lines indicate U^{6+}-planes, broken lines U^{5+}-planes, and dotted lines U^{5+}- (or U^{4+}-) planes. (*a*) corresponds to U_3O_8 (Figs. 2 and 4(*a*)), and (*d*) to U_3O_{8-x} at the final stage (Figs. 8 and 4(*d*)). The M values are ∞, 3, 2, and 1 from left to right. Actually, the distances between adjacent U-planes are not constant.

The structure of the final stage (Figs. 8, 4(*d*), and 12(*d*)), where $M=1$, is no more an out-of-step structure, but a new unique one. The spacing between nearest U^{6+}-planes in Fig. 12(*d*), i.e. ~ 8 Å, may be the *b*-value of this new structure, expressed in the orthorhombic system. It is supposed, however, that a more complicated manner of valency conversions and positional changes of uranium ions, but with the same arrangement of U^{6+} ions as above, can occur in the crystal under reduction without any essential modifications of the diffraction patterns. Therefore, ~ 8 Å may also be the *b*-value of a subcell of the new structure. Although the relation of the subcell to the true unit cell is unknown at present, it is interesting that Rundle *et al.* (1948) and Hoekstra *et al.* (1955) obtained both $b=\sim 32$ Å, i.e. four times ~ 8 Å, for an orthorhombic U_3O_{8-x} crystal. The present authors believe that a peculiar change in X-ray diffraction pattern of U_3O_8 under reduction, pointed out by Rundle *et al.* (1948) and Hoekstra *et al.* (1955) with no interpretations, has been here elucidated, at least in outline.

The final stage corresponds presumably to the lower limit of the U_3O_8 phase in the phase diagram of the system UO_2–U_3O_8. The diagram has been much discussed, and the reviews are given by Belle (1958) and by Runnalls (1959). Now, if U^{6+} is reduced to U^{4+}, the composition of the final stage becomes U_2O_5, coinciding exactly with that of an orthorhombic form obtained by Rundle *et al.* (1948). On the other hand, if U^{6+} is reduced to U^{5+}, it becomes U_8O_{21} ($=UO_{2.625}$), in accord with $UO_{2.62}$ obtained by Grønvold (1955). Since the composition at this composition limit is still in some doubt, a more detailed discussion on this point must be postponed.

It was mentioned before (see results) that the deviation from being hexagonal becomes pronounced as the reduction proceeds; the acute angle between a and a_2 of Fig. 3 is 60·7° for Fig. 2, and 61·0° for Fig. 8. On the other hand, the lattice constants obtained by many authors for orthorhombic U_3O_8 and U_3O_{8-x} at the composition limit are listed in Table 3, p. 362, of the report by Grønvold (1955). From this table, together with the lattice constants for U_3O_8 by Andresen (1958) and by Chodura & Malý (1958), the mean value of the angle in question for both orthorhombic crystals can be calculated. It amounts to 60·7° for U_3O_8, and to 60·5° for U_3O_{8-x}, implying that the angle approaches to 60° by the reduction, in contrast to the present result. The reason for this discrepancy is not known at present.

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Note added in proof. — The structure of cubic U_4O_9 proposed recently by Belbeoch *et al.* (1960) is, in our words, an out-of-step structure, where $M_x = M_y = M_z = 1$. In contrast to our case of U_3O_{8-x}, where the out-of-step mode is expressed by a translation vector, in the U_4O_9 structure it is expressed by a rotatory inversion $\bar{4}$. At any rate, we beliewe that long spacings resulting from out-of-step phenomena will be of great importance for understandig thoroughly the phase diagram of U-O system. One of the physical reasons underlying these structures lies probably in variable valency of uranium.

References

Andresen, A. F. (1958). *Acta Cryst.* **11**, 612.

Belbeoch, B., Piekarski, C. & Perio, P. (1960). *Bull. Soc. franç. Minér. Crist.* **83**, 206.

Belle, J. (1958). *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy*, Vol. 6, p. 569 (P/2404). Geneva: United Nations.

Chodura, B. & Malý, J. (1958). *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy*, Vol. 28, p. 223 (P/2099). Geneva: United Nations.

Doi, H., Takashima, A. & Suehiro, Y. (1960). Read at the Annual Meeting of *Phys. Soc., Japan*, April.

Fujiwara, K. (1957). *J. Phys. Soc. Japan*, **12**, 7.

Glossop, A. B. & Pashley, D. W. (1959). *Proc. Roy. Soc.* A, **250**, 132.

Grønvold, F. (1955). *J. Inorganic and Nuclear Chem.* **1**, 357.

Hirabayashi, M. & Ogawa, S. (1957). *J. Phys. Soc. Japan* **12**, 259.

Hoekstra, H. R., Siegel, S., Fuchs, L. H. & Katz, J. J. (1955). *J. Phys. Chem.* **59**, 136.

Ogawa, S. (1958). *Nippon Buturi Gakkai-Shi*, **13**, 609. (In Japanese).

Ogawa, S., Hirabayashi, M. & Watanabe, D. (1955). *Acta Cryst.* **8**, 510.

Ogawa, S. & Watanabe, D. (1954). *J. Phys. Soc. Japan*, **9**, 475.

Ogawa, S., Watanabe, D., Watanabe, H. & Komoda, T. (1958). *Acta Cryst.* **11**, 872.

Ogawa, S., Watanabe, D., Watanabe, H. & Komoda, T. (1959). *J. Phys. Soc. Japan*, **14**, 936.

Okuzumi, H., Perio, P. & Tournarie, M. (1959). *Acta Cryst.* **12**, 1039.

Perio, P. & Tournarie, M. (1959*a*). *Acta Cryst.* **12**, 1032.

Perio, P. & Tournarie, M. (1959*b*). *Acta Cryst.* **12**, 1044.

Raether, H. (1957). *Handbuch der Physik*, Vol. 32, p. 513. (Ed. by Flügge, S.). Berlin: Springer.

Rundle, R. E., Baenziger, N. C., Wilson, A. S. & McDonald, R. A. (1948). *J. Amer. Chem. Soc.* **70**, 99.

Runnalls, O. J. C. (1959). *Nuclear Fuel Elements*, p. 228. (Ed. by Hausner, H. H. & Schumar, J. F.). New York: Reinhold.

Uchikoshi, H., Ishii, B., Suzuki, K. & Takahashi, S. (1960). Read at the Annual Meeting of *Phys. Soc. Japan*, April.

Watanabe, D. (1958). *J. Phys. Soc. Japan.* **13**, 535,

Watanabe, D. & Ogawa, S. (1956). *J. Phys. Soc., Japan*, **11**, 226.

Acta Cryst. (1961). **14**, 771

Kristalljustierung mit Röntgen-Bildverstärker

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Single crystals, approximately oriented by optical methods, may be adjusted in a few minutes by the use of X-ray image amplifiers. The adjustment may be done with an accuracy of a few minutes of arc without any dark adaption. The present state of development excludes the use of wavelengths longer than Mo $K\alpha$ radiation.

Mit dem Röntgen-Bildverstärker (Tewes, 1955) können ohne den Umweg über Röntgen-Filmaufnahmen oder Registrierkurven z. B. der Gitterbau von Einkristallen schnell kontrolliert, Textureinflüsse an polykristallinen Proben aufgezeigt und ein Überblick über das Röntgen-Interferenzbild gewonnen werden (Mühe & Weyerer, 1957). Ferner lassen sich Kristalle für das Laue- und Drehkristall-Verfahren auf diese Weise rasch und präzise justieren.

Bei unvollkommen justierten Einkristallen fallen Einzelreflexe, die durch Drehung des Kristalls nacheinander an identischen Netzebenen entstehen, oft nicht mehr genau zusammen; sie fächern trotz derselben Indizierung senkrecht zu ihrer Schichtlinie, z. B. zum Äquator, nach beiden Seiten hin auf. Diese Abweichungen nehmen im allgemeinen mit wachsendem Braggschen Reflexionswinkel zu (v. Heimendahl & Weyerer, 1959).