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Crystallographic Out-of-Step in Oxygen-Deficient U_3O_8

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The previous electron diffraction investigation of the reduction of U_3O_8 to U_3O_{8-x} (R. Sato: Nature **188** (1960) 222. R. Sato, H. Doi, B. Ishii and H. Uchikoshi: Acta Cryst. **14** (1961) 763) showed that it is accomplished in a particular manner of crystallographic out-of-step. In connection with this, electron microscopic direct observations of arrangements of the out-of-steps in U_3O_{8-x} crystals are carried out. The results obtained are in accordance with the out-of-step structures deduced from the previous work.

It was shown previously[1),2)] that the reduction of U_3O_8 to U_3O_{8-x}, where x is a small positive variable, is accomplished in a particular manner of crystallographic out-of-step. Since the out-of-step structures reported hitherto are confined mainly to physically ordered states of binary alloys, this constitutes a new case of this kind of structure, which is related to chemical decomposition.

In Figs. 1 and 2 the electron diffraction patterns of U_3O_8 and U_3O_{8-x} are respectively reproduced. The mode of out-of-step required for interpretation of spot splittings, such as in Fig. 2, was discussed in one of the previous papers[2)] in some detail. The outline is as follows.

The out-of-step concerned is 'unidirectional,' i.e. at a given small portion of the crystal the boundary planes between out-of-step domains are parallel to each other, all being most likely (010). The physical phenomenon causing such out-of-step structures lies in slight positional changes of uranium ions accompanying a particular mode of valency

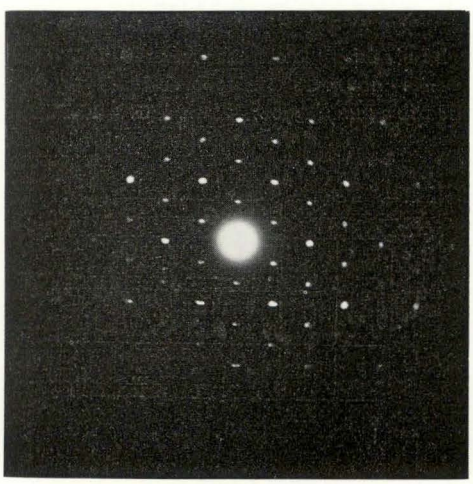

Fig. 1. Electron diffraction pattern of a single crystal of orthorhombic U_3O_8. The crystal is very thin along [001]. The beam is along [001]. The vertical direction is [010].

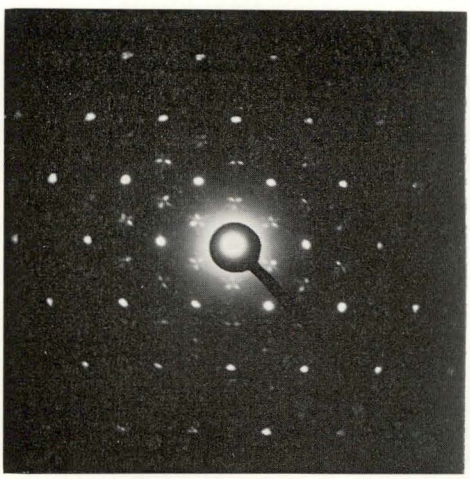

Fig. 2. Electron diffraction pattern of U_3O_{8-x} obtained by reduction of the sample of Fig. 1. The spot splitting becomes more pronounced as the reduction proceeds further.

conversions (U^{6+} to U^{5+} or U^{4+}, and U^{5+} to U^{6+}); successive stages of line-up of U-planes with respect to [010] in the course of reduction are schematically depicted in Fig. 3. Note that actually U^{5+}- (or U^{4+}-) planes trisect (or divide into four equal parts) only approximately the spacing between adjacent U^{6+}-planes, and, moreover, that the spacing between adjacent U^{6+}-planes is either 1 or 4/3 (taking the spacing in Fig. 3 (a) as the unit). Thus, the intermediate stages constitute out-of-step structures, where an out-of-step takes place at every M-th step of the U^{6+}-plane. It is readily understood that M decreases as the reduction proceeds, since smaller M means lower density of the U^{6+}-plane in the crystal.

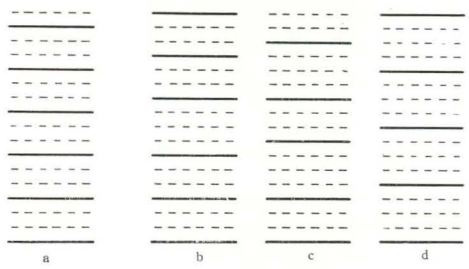

Fig. 3. Sequence of particular valency conversions of uranium ions in the reduction of U_3O_8 to U_3O_{8-x}. Solid lines: U^{6+}-planes. Broken lines: U^{5+}-(or U^{4+}-) planes. (a) corresponds to U_3O_8 (Fig. 1). The M values are ∞, 3, 2 and 1 from left to right.

Fig. 4. Electron diffraction pattern of U_3O_{8-x} showing split spots and satellites. Enlarged about twice as compared with Figs. 1 and 2.

The asymmetric spot splittings in the direction above-below in the patterns, such as Fig. 2, can be accounted for by such out-of-step structures, the amount of splitting depending on the value of M. Actually the split spots in Fig. 2 are arranged in a triad symmetry around the original position. This is due to the presence of inherent twins, oriented at 60° to each other around [001].

In another example of diffraction pattern of U_3O_{8-x} (Fig. 4), weaker satellites around *normal* spots are observed in addition to the above split spots (the satellites around the undeviated spot are masked by the strong back ground). Although these satellites may result from a certain periodic lattice modulation[3], their positions are compatible with the consideration of double diffraction, as shown in Fig. 5.

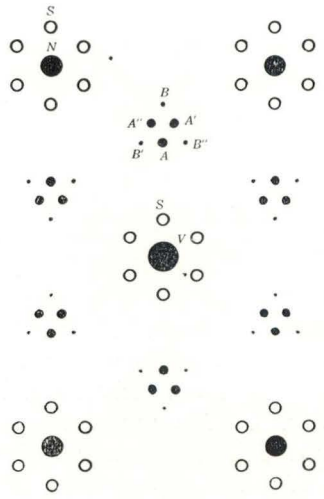

Fig. 5. Schematic depiction of diffraction spots due to U_3O_{8-x}. U: undeviated spot. N: a *normal* spot. A, B, etc.: split spots. Open circles: satellites. Note that the distance US (or NS) is equal to the distance AB.

Now, since the average spacing between adjacent U-planes in Fig. 3 is $\sim$2Å[4),5)], the spacing between adjacent out-of-steps in the crystal under reduction is $\sim 2(3M+1)$Å. Such spacings will be directly observed by electron microscopy, if they exceed the limit of the resolving power. The direct observation seems, however, to be more difficult than in cases of ordered binary alloys[6),7)]. The exposure required is quite long, since the in-

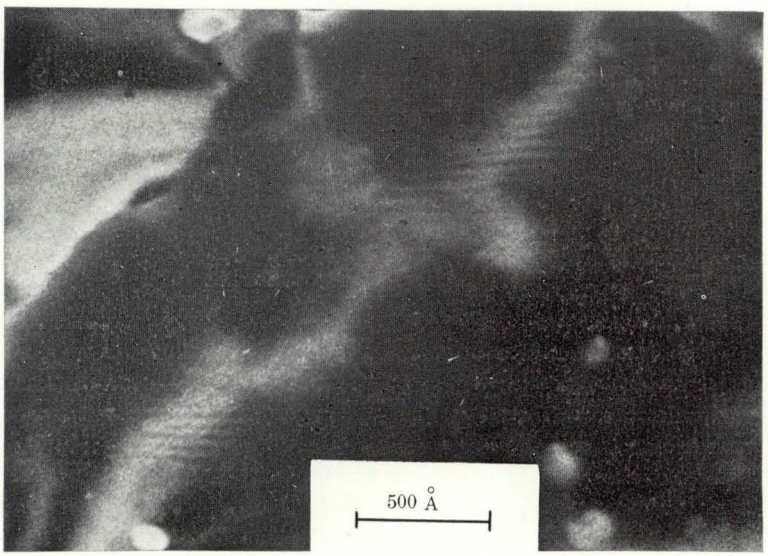

Fig. 6. Electron micrograph of a U_3O_{8-x} crystal.

cident beam must be sufficiently weak to avoid proceeding of the reduction. Moreover, with ordered binary alloys two spots of a splitting pair are equal in intensity, conditioning high contrasts of the dark-field image[7] which is formed by the combination of the two diffracted beams. With U_3O_{8-x} this can not be expected, since the two spots are remarkably different in intensity.

An example of electron micrograph, where parallel streaks are clearly seen, is reproduced in Fig. 6. The apparatus used was of JEM-5Y-type of Japan Electron Optics Laboratory. In this example streaks parallel to (010) are almost equidistant, the distance being consistent with the amount of the spot splitting in the corresponding diffraction pattern. Usually, however, the spacing is not uniform within a group of streaks. This is most likely responsible for the elongation of split spots along the splitting direction (Figs. 2 and 4).

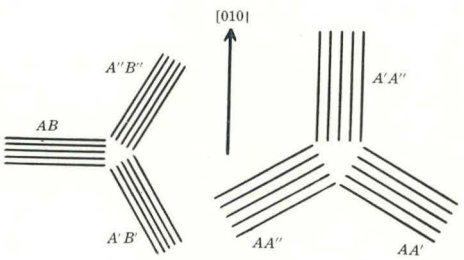

Fig. 7. Relative orientations of groups of parallel streaks arising from the combinations of indicated diffracted beams.

The streaks in Fig. 6 seem to be caused by the combination of the diffracted beams A and B (Fig. 5). Since, however, A' and B', and A'' and B'' are also to be combined, groups of parallel streaks, which make 120° (or 60°) to each other, are expected to be observed at different portions of a single micrograph. They are schematically shown in Fig. 7, and lettered AB, $A'B'$, and $A''B''$, respectively. This expectation has been confirmed by observation of many micrographs obtained.

In rare cases, however, other kinds of groups of parallel streaks, which make 30° (or 90°) with, for example, the AB group, have been observed (Fig. 7). In them the streak spacing is approximately $\sqrt{3}$ times as large as that of AB group. These groups are supposed to arise from the situation that the upper and lower halves of the sample are oriented in the twin relation. In such a case parallel streaks with the above spacing can arise as the result of the combinations of A and A', A' and A'', and A and A'' (if B, B', and B'' are ignored because of their

weakness in intensity).

Thus, the results of the present electron microscopic direct observation support the out-of-step structure of oxygen-deficient U_3O_8, which was previously deduced from the analysis of electron diffraction patterns.

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DISCUSSION

J. D. H. Donnay: I would like to make some remarks that may be of general crystallographic interest on the relationship between antiphases and twinning. By definition a crystal must be homogeneous, at least on the scale of optical microscopy. A twin is composed of crystals (not the other way round). An edifice composed of antiphase domains, although heterogeneous on the structural scale, would still be homogeneous on the large scale and thus could still be called a crystal.

A twin operation has been, traditionally, a point-group operation. If the twinning theory is extended by making it a space-group operation, one finds that among the operations that will raise the symmetry of a space group to that of a higher space group, some will lead to twinning, others to antiphases.

R. Sato: I should say that the term 'anti-phase structure' is rather a misnomer for my case. There are three kinds of domains with respect to phase instead of two kinds of domains in the case of binary alloys.

S. Ogawa: The problem treated by Dr. Sato concerns not the anti-phase structure but the out-of-step structure, I think.