

des enchaînements suivant la rangée [210]. Il n'y a pas de liaisons hydrogène entre ces chaînes, les contacts se faisant par des liaisons de van der Waals.

La densité élevée des cristaux d'EDTA ( $1,64 \text{ g.cm}^{-3}$ ), qui peut être comparée à celle du NTA ( $1,66 \text{ g.cm}^{-3}$ ) ainsi d'ailleurs qu'une très faible solubilité dans l'eau sont des manifestations de ces fortes liaisons hydrogène.

### (c) Configuration de la molécule

Les structures cristallines des sels de rubidium et de potassium de l'EDTA montrent que l'ion  $\text{H}_2\text{Y}^{2-}$ , où Y représente le tétra-anion de l'EDTA de formule  $[\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2]_2$ , s'y présente sous deux conformations différentes, correspondant à deux sortes d'interactions  $\text{NH}^+ \cdots \text{OOC}$  chélatées:

pseudosymétrie  $2/m$  avec des liaisons hydrogène bifides pour le sel de rubidium;

pseudosymétrie 2 avec des liaisons hydrogène trifides pour le sel de potassium.

L'acide EDTA,  $\text{H}_4\text{Y}$ , possède un axe de symétrie binaire 2, et présente des liaisons hydrogène trifides chélatées, différentes du sel de potassium, puisque tous les groupements carboxyliques n'y sont pas ionisés. Cette grande liberté de conformation permet d'expliquer la tendance des ions de l'EDTA à former des complexes très stables de conformation variable avec un grand nombre d'ions métalliques.

Ainsi dans les complexes  $\text{Fe(III)(H}_2\text{O)HY}$ , l'ion  $\text{HY}^{3-}$  est-il pentacoordonné à l'ion ferrique (Hoard, Kennard & Smith, 1963) alors qu'il se trouve être hexacoordonné aux ions  $\text{Co(III)}$  et  $\text{Ni(II)}$  dans les complexes  $\text{CoY}^-$  et  $\text{Ni(H}_2\text{Y)H}_2\text{Y}$  (Weakliem & Hoard, 1959; Smith & Hoard, 1959).

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## Analysis of the Superstructure of $\text{U}_4\text{O}_9$ by Neutron Diffraction

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The superlattice structure of  $\text{U}_4\text{O}_9$  at room temperature is cubic (space group  $I4_132$ ), with the cell dimension  $21.76 \text{ \AA}$ , which is 4 times that of the fundamental structure of  $\text{U}_4\text{O}_8 (= \text{UO}_2)$ . Structure analysis was made with single-crystal neutron diffraction from the  $hk0$  superlattice reflexions. The arrangement of 64 additional oxygen atoms in the superlattice and the displacements of the uranium atoms from the positions in the fluorite-type fundamental structure are determined. Forty of the 64 additional oxygen atoms are located at the centres of interstices formed by cubes of oxygen atoms in a fluorite-type structure. The remaining 24 atoms are displaced from the centres of the interstices by  $0.52 \text{ \AA}$  along the face-diagonal directions. Of the 256 uranium atoms constituting the fluorite-type structure, 16 are found to be displaced by  $0.45 \text{ \AA}$  along the body-diagonal directions from their normal positions.

### 1. Introduction

Alberman & Anderson (1949) pointed out that there is a new phase of uranium oxide, with oxygen content slightly higher than in  $\text{UO}_2$ , whose structure is closely related to the fluorite-type structure of  $\text{UO}_2$ . This phase was identified as  $\text{U}_4\text{O}_9$  by Hering & Perio (1952).

The structural investigations on  $\text{U}_4\text{O}_9$  were made with X-ray (Belbeoch, Piekarski & Perio, 1961),

neutron (Willis, 1964) and electron diffraction (Blank & Ronchi, 1968). In addition to the fundamental reflexions appropriate to the fluorite-type structure, many superlattice reflexions were observed, suggesting long-range order in the arrangement of the additional oxygen atoms and also displacements of some of the uranium atoms. The superlattice reflexions are found to correspond to a cubic lattice with the unit translation  $a$ , which is four times that of the fluorite-type  $\text{UO}_2$

structure, *i.e.*  $a=4 \times a_0$ ,  $a_0$  being the lattice constant of the fundamental structure.

From the X-ray observations of superlattice reflexions from a  $U_4O_9$  single crystal, Belbeoch *et al.* (1961) concluded that the space group is  $I\bar{4}3d$  for the  $4 \times a_0$  superstructure, and proposed a structural model on the basis of symmetry considerations. Willis's (1964) neutron study, which was concerned only with the fundamental reflexions, yielded the structure of a 'composite cell' which in his definition, corresponds to an average for 64 substructures in a  $4 \times a_0$  superlattice cell. However, a significant inconsistency was found between the results of Belbeoch *et al.* (1961) and those of Willis (1964) with regard to the positions of the additional oxygen atoms. Moreover, electron diffraction studies of  $U_4O_9$  thin-films by Blank & Ronchi (1968) showed a characteristic arrangement of the superlattice reflexions, which proved inconsistent with that which appeared in the X-ray observations by Belbeoch *et al.* (1961). However, a structure determination was not made because of the limitations in quantitative intensity measurements.

The object of the present work with X-ray and neutron diffraction was to establish a model for the superstructure of  $U_4O_9$  by means of quantitative analysis of the superlattice reflexions.

## 2. Experimental

A single-crystal specimen was prepared by oxidation of a single crystal of  $UO_2$  as follows (Masaki & Ishii, 1970). Single crystals of  $UO_2$  produced by arc-fusion were purified in a stream of hydrogen gas at  $1000^\circ\text{C}$  for 10 hours, and then mixed with  $UO_2$  powder in a weight ratio: single crystal/powder =  $\frac{1}{3} \sim \frac{1}{7}$ . The mixture was placed in a silica tube together with  $U_3O_8$  powder, so that the oxygen atoms released by thermal dissociation of  $U_3O_8$  diffused into the  $UO_2$  single crystals. The ratio of total quantity of  $UO_2$  to that of  $U_3O_8$  was adjusted exactly to 1:1.6033, so that all the uranium oxide was changed completely into  $U_4O_9$ . The silica tube was evacuated to  $10^{-3}$  torr and then sealed. The tube was heated up to  $1050^\circ\text{C}$  from room temperature in an electric furnace at the rate of  $6.5 \sim 7.0^\circ\text{C/hr}$ . The temperature was maintained at  $1050^\circ\text{C}$  for four weeks, and then brought down to room temperature at a cooling rate of  $6.5 \sim 7.0^\circ\text{C/hr}$ .

Three different specimens of  $U_4O_9$  were thus obtained under exactly the same conditions.

(a) A single crystal, 420 mg in weight, of an irregular shape with a linear dimension of about 5 mm.

(b) Thinner crystals of various habits with linear dimensions ranging from 0.3 to 0.8 mm.

(c) Powders.

X-ray examination was made mainly on the specimens (b) and (c), while specimen (a) was used for the neutron diffraction experiment. Oscillation and Weissenberg photographs of the specimens (b) showed faint but sharp superlattice spots, which could be indexed

on the basis of a superlattice whose cell edge is four times that for the fluorite-type fundamental structure. The precise measurement of lattice parameters, made with the specimen (c) using Debye-Scherrer photographs, gave  $a_0 = 5.4410 \pm 0.0005 \text{ \AA}$ , which agreed well with the published values of  $a_0$  (Grønvold, 1955; Belbeoch, Laredo & Perio, 1964; Ishii, Naito, Oshima & Hamaguchi, 1971). In the oscillation and Weissenberg photographs for specimen (a), there were no evidences for twinnings or parallel growths of crystals.

A systematic exploration of the (001) relplane of  $U_4O_9$  by thermal neutrons was performed at room temperature, with a 2-circle, off-line controlled diffractometer (Minakawa, Sakamoto & Hamaguchi, 1968) installed at the JRR-2 (10 MW,  $10^{14} \text{ n.cm}^{-2}.\text{sec}^{-1}$ ) reactor of JAERI. Neutrons with wavelength  $1.00 \text{ \AA}$  from a transmission-type Cu (111) monochromator were used. The  $\lambda/2$  contamination was estimated as 0.13% by the diffraction intensities of a  $UO_2$  single

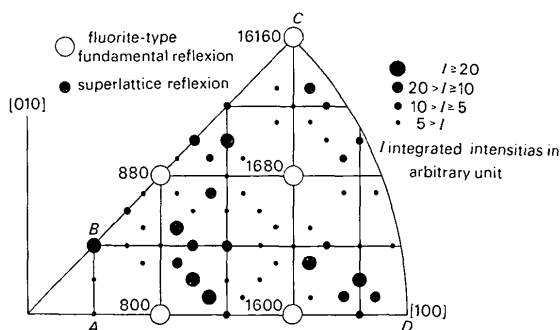


Fig. 1. (001) relplane of  $U_4O_9$  as observed by neutron diffraction.

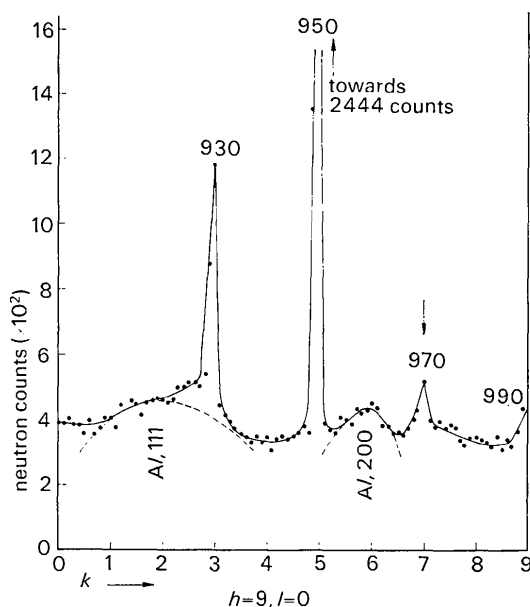


Fig. 2. Scanning record along the reciprocal line  $x^* = 1/a \times 9$ . Debye-Scherrer profiles of the aluminum rod supporting the crystal are seen in the background.

crystal. Off-line control of the diffractometer with an IBM 7044 computer was used, so that the superlattice reflexions indicated in Fig. 1 were systematically recorded. The scan was made in the area of *ABCD* in Fig. 1, along the relrods parallel to the [010] axis; *i.e.* along the lines

$$x^* = \frac{1}{a} \times m = -\frac{1}{4a_0} \times m, \quad (1)$$

where *a* and *a*<sub>0</sub> are the unit translations of the superlattice and fundamental lattice respectively, and *m* is an integer between 4 and 22. A stepwise scan was made at intervals of  $\frac{1}{10} \times \frac{1}{a} = 0.0046 \text{ \AA}^{-1}$  in the vicinity of each superlattice point. A typical scan record for *m*=9 [equation (1)] is reproduced in Fig. 2. The (001) rel-plane of U<sub>4</sub>O<sub>9</sub> as observed in this way is shown in Fig. 1, where the solid circles represent the superlattice reflexions with their radii roughly proportional to the observed integrated intensity, and the open circles the reflexions from the fluorite-type fundamental structure.

### 3. Structure analysis

#### 3.1 Space group

From the observed superlattice points (Fig. 1), an extinction rule of *h*=4*n* for *h*00's was derived in addition to *h*+*k*+*l*=2*n* for *hkl*'s. The space group was thus concluded to be *I*4<sub>1</sub>32 for the superlattice structure. Besides the superlattice reflexions described already, a few weak, but distinct, peaks corresponding to an 8 × *a*<sub>0</sub> superstructure were also observed between

the superlattice reflexions (Masaki & Doi, 1968). These reflexions, however, will be neglected in the following analysis. The above result differs from that of the X-ray study by Belbeoch *et al.* (1961), who assigned the space group *I*43*d* on the basis of the extinction of *hhl* with 2*h*+*l*=4*n*. This extinction apparently contradicts the present observations (Fig. 1), in which the superlattice reflexions 770 and 990 definitely exist.\* Contradiction occurs also on the [100] relrod, where Belbeoch *et al.* observed no superlattice reflexions. As seen in Fig. 1, the present results show the existence of *h*00 reflexions with *h*=4*n*, *e.g.* 400, 12,0,0 and 20,0,0.

From the neutron diffraction by a single crystal of U<sub>4</sub>O<sub>9</sub>, Willis (1964) reported that the superlattice reflexions *hkl* with *h*,*k*,*l*=4*n* were scarcely observed. These observations are also inconsistent with the present result, as shown in Fig. 1, where the reflexions such as 440, 840, 12,4,0, *etc* evidently exist.

The results of the electron diffraction study on U<sub>4</sub>O<sub>9</sub> thin-films by Blank & Ronchi (1968), are in agreement with those of Fig. 1, as far as the arrangement of superlattice points is concerned. Exceptions occur, however, with regard to the superlattice points 970 (arrow in Fig. 2), 17,1,0, 770 and 990, which Blank & Ronchi attributed to some trivial causes such as double reflexion, thin-film effect *etc*. The present neutron study indicates that these reflexions, though very weak, are the ones really appropriate to the superlattice structure.

\* These superlattice reflexions were also observed by a conventional  $\theta$ -2 $\theta$  scan along  $\langle 110 \rangle$  (Masaki *et al.*, 1968).

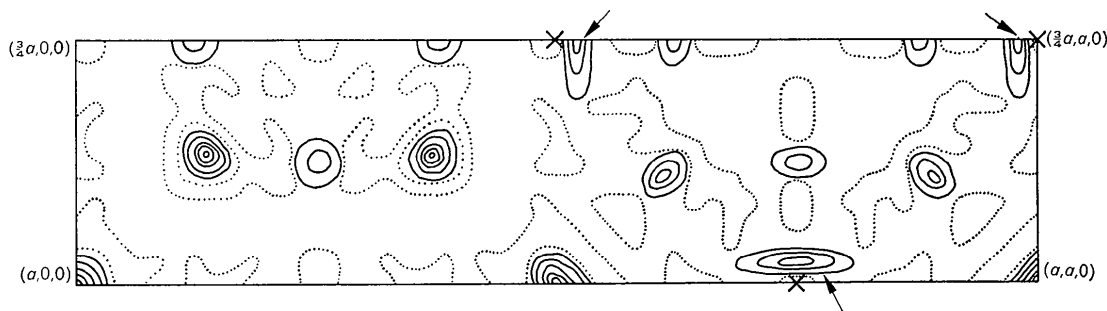


Fig. 3. Difference Fourier synthesis of 4 × *a*<sub>0</sub> superstructure projected onto (001) plane. Zero level is indicated by broken contours. Arrowed peaks indicate the uranium atoms displaced from their positions in the fluorite-type mother structure shown by crosses. Other peaks are additional oxygen atoms.



Fig. 4. Final difference Fourier synthesis of 4 × *a*<sub>0</sub> superstructure projected onto the (001) plane, with the displacement of uranium atoms taken into account (compare with Fig. 3).

### 3.2 Structure analysis

The characteristic arrangement of superlattice spots around each of the fundamental relops in Fig. 1 appears to obey the extinction rule appropriate to the positions 8(a), 8(b), 12(c) and 12(d) of the space group  $I4_132$  (*International Tables for X-ray Crystallography*, 1952). Thus 40 of the 64 additional oxygen atoms were tentatively placed at these special positions, and a difference Fourier synthesis was made correspondingly.\* This synthesis revealed additional peaks for the remaining 24 oxygen atoms at the positions 24(g). The parameter  $x$  of these positions was then varied, and the best fit between the observed and calculated  $F$ 's was found at  $x=0.108$ .†

Difference Fourier synthesis at this stage showed that some of the uranium atoms were displaced from the positions in the fluorite-type structure to the position 16(e) of  $I4_132$ , as indicated by the arrows in Fig. 3. The most probable value of the parameter  $x$  for the 16(e) positions was determined from the variation of  $x$ , and the result  $x=-0.012$  was obtained. Fig. 4 shows the final difference Fourier synthesis for the superlattice reflexions; the signs here were determined by taking account of the arrangement of the additional oxygen atoms and the displacement of the uranium atoms. The structure obtained is represented schematically in Fig. 6(a), where only 64 additional oxygen atoms and 16 displaced uranium atoms are shown.

\* Although the space group  $I4_132$  has no centre of symmetry, its projection onto the (001) plane is centrosymmetric, so that the phase assignment for  $hk0$  reflexions could be made with relative ease. Only the superlattice reflexions were included in the difference Fourier synthesis. The differences in  $|F|$ 's for fundamental reflexions of  $U_4O_9$  and  $U_4O_8$  were found to be too delicate to estimate experimentally, as they are small differences between two very large quantities (see also the footnote in the next column).

† The precision of the parameter  $x$ , for the 24(g) and 16(e) positions, was estimated as  $\pm 0.0005$ . Atomic positions and distances described below are thus subject to errors of the order of  $\pm 0.01$  Å. All the computations of the structure factors as well as the Fourier syntheses were carried out on an IBM 7044 computer with the programs written by one of us (NM).

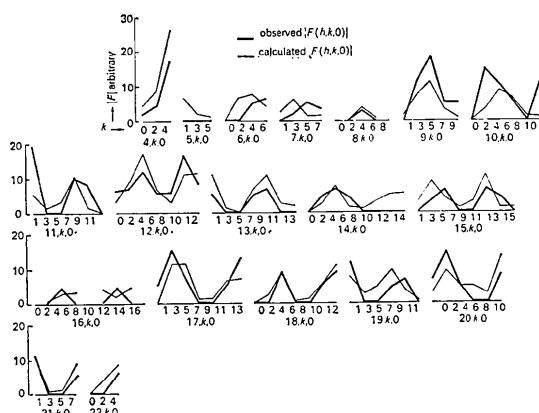


Fig. 5. Comparison of observed and calculated  $|F(hk0)|$ 's of superlattice reflexions.

The calculated and the observed superlattice structure factors are compared in Fig. 5, where the agreements are fairly satisfactory. The scattering lengths used for uranium and oxygen were  $b_U=0.85 \times 10^{-12}$  cm and  $b_O=0.577 \times 10^{-12}$  cm respectively (Bacon, 1962). Temperature factors were not taken into account, as from a Wilson (1949) plot, they were estimated to be very small. Although the  $R$ -value ( $=\sum ||F_{obs}| - |F_{calc}|| / \sum |F_{obs}|$ ) for the superlattice reflexions was still as high as 49% at this stage of analysis but it should be noted that the intensities of the superlattice reflexions are very weak\* and subject to relatively high experimental errors. As pointed out by Lipson & Cochran (1957), for a structure giving a large number of very weak reflexions, the  $R$  value may be large without disproving the correctness of the structure model. In fact, the  $R$  value decreased to 20% or less when only three fundamental reflexions were taken into account, together with the superlattice reflexions.

### 4. Description and discussion of the superstructure

The coordinates of the 64 additional oxygen atoms and the 16 displaced uranium atoms are shown in Table 1. The origin is taken at the symmetry centre in the (001) projection, that is, it is shifted by  $(\frac{1}{2}, \frac{1}{2}, 0)$  from the origin adopted in *International Tables for X-ray Crystallography* (1952). Fig. 6(a) illustrates the arrangement of those atoms which are responsible for the superlattice reflexions. Atoms belonging to the fundamental structure and contributing only to the fundamental reflexions are ignored. The superstructure is represented as a regular sequence of 4 layers. A layer consists of  $4 \times 4 \times 1$  substructures, each of which is derived from the fluorite-type structure of  $UO_2$  as described in the following. Each substructure is specified as in Fig. 6(b), where the shaded substructure is designated as  $(l, m)$  of the  $n$ th layer,  $l$  and  $m$  are the numbering for the substructures in a layer, and  $n$  that of a layer ( $1 \leq l, m, n \leq 4$ ).

Table 1. The coordinates of the 64 additional oxygen atoms and of 16 displaced uranium atoms

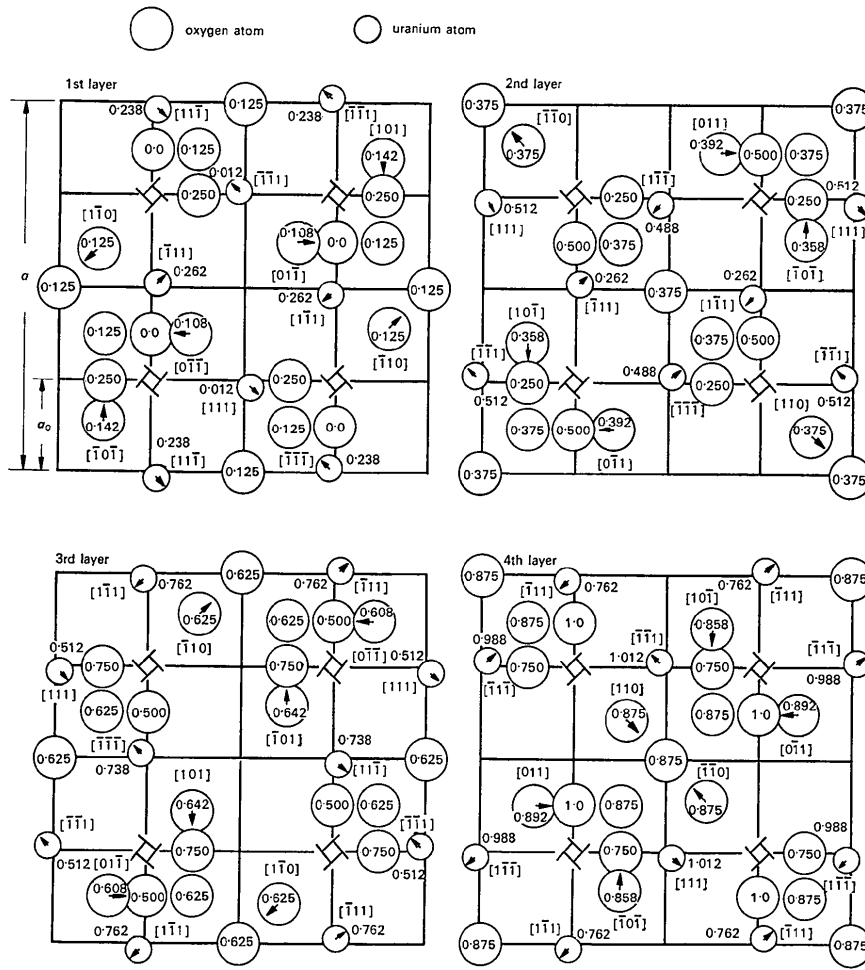
The origin is shifted by  $(\frac{1}{2}, \frac{1}{2}, 0)$  from that of *International Tables for X-ray Crystallography* (1952). O(2) is the oxygen atom positioned in the centre of the interstices, O(3) is that displaced from the centre of the interstices in the face-diagonal directions. U(2) is the uranium atom displaced along the body-diagonal directions from its site in the fluorite-type structure.

O(2):	8(a)	-0.375	-0.125	0.125
O(2):	8(b)	0.375	-0.375	0.875
O(2):	12(c)	-0.375	-0.250	0.250
O(2):	12(d)	0.125	-0.250	0.250
O(3):	24(g)	-0.375	-0.142	0.358
U(2):	16(e)	0.488	0.262	0.988

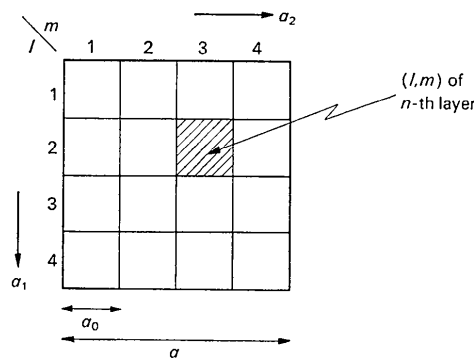
\* For most of the superlattice reflexions, integrated intensities are as weak as one-thousandth of those of the fundamental reflexions.

The fluorite-type structure of  $\text{UO}_2$  ( $=\text{U}_4\text{O}_8$ ) may be considered as the mother structure for the superlattice structure of  $\text{U}_4\text{O}_9$ . The unit cell of this mother structure contains eight small cubes composed of oxygen atoms, with the cube edge of  $\frac{1}{2}a_0$ ,  $a_0$  being the cell edge

of the mother structure ( $a_0 = \frac{1}{4}a$ ). Four of these cubes form a tetrahedron with a uranium atom at the centre. The other four do not have the central uranium atom, thus providing room for an additional oxygen atom (Belboech *et al.*, 1961; Willis, 1964). In fact, of the 64



(a)



(b)

Fig. 6. (a) Arrangements of additional oxygen and displaced uranium atoms in the  $4 \times a_0$  superlattice, projected onto the  $(001)$  plane. Arrows in the circles indicate the directions of the displacement of the relevant atoms. (b) Labelling of the substructures making up the  $4 \times a_0$  superstructure.

additional oxygen atoms in the  $4 \times a_0$  superstructure, 40 atoms at 8(a), 8(b), 12(c) and 12(d) positions (Table 1) are found at the centres of these cubes, whereas the remaining 24 atoms at 24(g) position are displaced by 0.52 Å from the centres in the face-diagonal directions. The additional oxygen atoms inserted into the interstices seem to affect the initial skeleton of the fluorite-type structure of  $UO_2$ . Thus of the 256 uranium atoms in the  $4 \times a_0$  superstructure, 16 atoms at 16(e) are displaced by 0.45 Å in the body-diagonal directions.

The structural relations between the  $U_4O_9$  superstructure and the fluorite-type  $UO_2$  ( $=U_4O_8$ ) mother structure may be best illustrated by the atomic arrangements in the  $\{110\}$  sections of these structures. The  $\{110\}$  section of  $UO_2$  structure is shown in Fig. 7(a), where U(1) and O(1) are the uranium and oxygen atoms constituting the fluorite-type structure which are discarded in Fig. 6(a). Substructures unaffected by the additional oxygen atoms, which are shown in Fig. 7(a), are found at, e.g. the (4, 4) substructure of the 1st layer in Fig. 6(a). Insertion of additional oxygen atoms O(2) at the positions 8(a), 8(b), 12(c) and 12(d), which correspond to the centres of interstices formed by small cubes of oxygen atoms, gives the substructure illustrated in Fig. 7(b); this structure is found for the (3, 1) substructure of the 1st layer [Fig. 6(a)], for example. The distance between the inserted and host oxygen atoms is found to be 2.37 Å (Table 2), which suggests that no groupings of atoms like O-O, O-O-O, etc. are formed, because the diameter of the oxygen atom usually adopted for the stoichiometric U-O compounds (ca. 2.6 Å) is not much different from the observed O(1)-O(2) distance of 2.37 Å.

Table 2. Interatomic distances of the nearest neighbours O-O, O-U and U-U

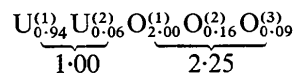
O(1) and U(1) mean the oxygen and uranium atoms incorporated in the fluorite-type mother structure. Other symbols have the same meanings as in Table 1.

O(1)-O(1)	2.72 Å	O(1)-O(2)	2.37 Å
		O(1)-O(3)	1.96
O(1)-U(1)	2.37	O(1)-U(2)	1.92
U(1)-U(1)	3.85	U(1)-U(2)	3.49

The additional oxygen atoms O(3) at 24(g) are displaced from the centres of interstices in the face-diagonal directions. As seen in the (3, 4) substructure of the 1st layer [Fig. 6(a)], the  $\{110\}$  section of the substructure becomes as shown in Fig. 7(c), where the oxygen atoms O(1) and O(3) form a triplet O(3)-O(1)-O(3) with the distance O(1)-O(3) = 1.96 Å. Since no bond length O-O shorter than about 2.2 Å is found in  $UO_2$ ,  $U_3O_8$  or  $UO_3$  (Loopstra, 1964; Debets, 1966), the O(1)-O(3) distance here described is the smallest yet found in the U-O system, being about 25% lower than the usually accepted diameter of an oxygen atom. These structural features seem to be compatible with the result of Kingery (1965) obtained by thermodynamic experiments, that an oxygen

atom enters into the  $UO_2$  structure in a form of neither a single atom nor an ion but as a molecular or ionic complex. Such complexes of oxygen atoms are found in some other oxides, e.g.  $BaO_2$ ,  $\alpha-NaO_2$ ,  $\alpha-KO_2$  and  $CaO_2 \cdot 8H_2O$  with an O-O distance of about 1.5 Å (Wells, 1962). Some uranium atoms are found to be displaced in the body-diagonal directions as a result of the insertion of the oxygen atoms as shown in Figs. 7(d) and (e). These displacements occur alternately along a body-diagonal  $[111]$  of the superstructure starting, for example, from the (4, 3) of the 1st layer. The linear section of the superstructure along this diagonal is illustrated in Fig. 7(f).

The superstructure described above can be expressed by a formula:



where  $U^{(1)}$  and  $O^{(1)}$  mean the uranium and oxygen atoms constituting the fundamental structure of fluorite type,  $U^{(2)}$  is the uranium atom displaced by 0.45 Å from the position of the fluorite-type structure in the body-diagonal directions,  $O^{(2)}$  the additional oxygen atom inserted at the centre of the interstice formed by a cube of oxygen atoms, and  $O^{(3)}$  the additional oxygen atom displaced from the centre of the interstice by 0.52 Å in the face-diagonal directions.

The 'composite cell' derived by Willis (1964) is not compatible with the present result, not only with regard to the positions of the additional oxygen atoms in the

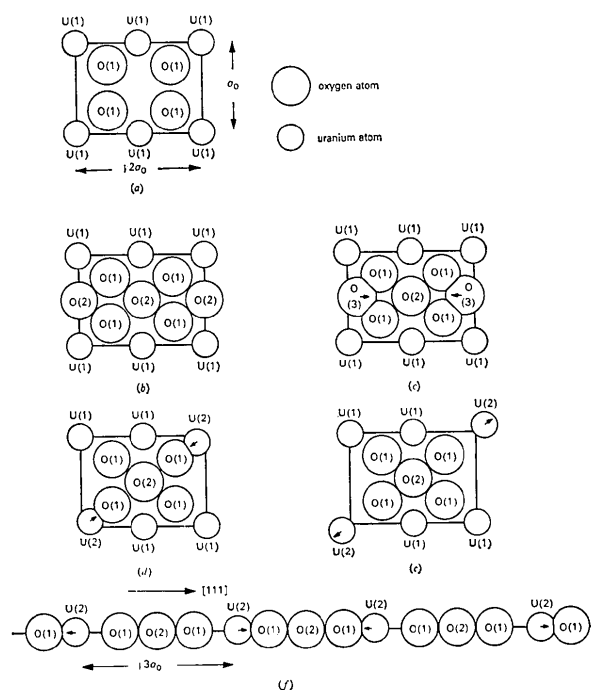


Fig. 7. Atomic arrangements in the  $\{110\}$  sections of the various substructures. Symbols O(1), O(2), O(3), U(1) and U(2) and the arrows in the circles have the same meanings as in Tables 1 and 2 and Fig. 6(a) respectively.

interstices but also in the fact that the displacements of the uranium atoms were entirely disregarded in his model. It should be noted that, in Willis's analysis, only the fundamental reflexions,  $hkl$  with  $h+k, k+l, l+h=8n$ , were taken into account, although the superlattice reflexions  $hkl$  with  $h, k, l=4n$  should be included together with the fundamental reflexions to obtain the 'composite cell structure' in his definition.\* Willis estimated the intensities of these superlattice reflexions to be negligibly weak, whereas the present observations revealed their presence with rather significant integrated intensities (for *e.g.* 440, 12,0,0, 12,4,0, 12,12,0, 20,0,0 *etc.* in Fig. 1). The discrepancies between the two models seem to be due to the differences in the intensity data and/or in the crystal structures examined in the two studies.

Belbeoch *et al.* (1961) described a superstructure model on the basis of the X-ray observation of superlattice reflexions. As discussed in § 3.1, the space group they proposed contradicts the present observation. In their model, all the additional oxygen atoms were simply placed at the centres of interstices, although they anticipated the possibility of their displacement.

The displacement of uranium atoms concluded by the present neutron study is compatible with an X-ray observation (Masaki & Ishii, 1970) in which many superlattice reflexions, though very weak compared with the fundamental ones, were observed with appreciable intensities that cannot be expected from the additional oxygen atoms alone. A recent study of the channelling of He<sup>+</sup> ions carried out by Matzke, Davies & Johansson (1971) gave further evidence for

the displacement of uranium atoms in the U<sub>4</sub>O<sub>9</sub> superstructure.

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\* It is derived from the superstructure by superimposing all the  $4 \times 4 \times 4$  substructures.

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## Structure Cristalline et Moléculaire du *p*-Nitrophényl-1 méthyl-3 bromo-4 pyrazole

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1-*p*-Nitrophenyl-3-methyl-4-bromopyrazole crystallizes in the space group  $Pna2_1$  in a unit cell of dimensions  $a=12.63$ ,  $b=21.58$ ,  $c=3.88$  Å. The unit cell contains four molecules. 1057 independent intensities were collected on a diffractometer by a  $\theta$ -scan method with Cu  $K\alpha$  radiation. The structure was refined by full-matrix least squares to a conventional  $R$  of 0.044. The structural features of this molecule are discussed.

Le *p*-nitrophényl-1 méthyl-3 bromo-4 pyrazole a été synthétisé dans le laboratoire de Monsieur le Professeur Jacquier (Elguero & Jacquier, 1966). Nous avons entrepris l'étude cristallographique de ce composé

pour préciser sa conformation moléculaire et pour pouvoir la comparer à celle du (dinitro-2',4'-phényl)-1 bromo-4 pyrazole (Galigné & Falgueirettes, 1969).