Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

New superlattice reflections of U_4O_9. By Norio Masaki and Kenji Doi, *Japan Atomic Energy Research Institute, Tokai, Japan*

Neutron reflexions corresponding to an $8 \times a_0$ ($a_0 = 5 \cdot 44$ Å) cubic superlattice were observed for a U_4O_9 single crystal at room temperature and at 120 °C.

Reflexions corresponding to an $8 \times a_0$ superlattice were observed for a U_4O_9 single crystal by means of neutron diffraction, in addition to $4 \times a_0$ superlattice reflexions described by Belbeoch, Piekarski & Perio (1961), where a_0 is the cube edge of the composite cell defined by Willis (1964).

A single crystal of UO_2, supplied by Spencer Inc., U.S.A., was sealed in an evacuated silica tube, with UO_2 and U_3O_8 powders whose quantities were so selected that the whole of the UO_2 crystal would be oxidized completely into U_4O_9. The tube was heated up to 1050 °C at a rate of $6 \cdot 5 \sim 7 \cdot 0$ °C per hr, kept at this temperature for about 4 weeks, and then cooled down to room temperature at $6 \cdot 5 \sim 7 \cdot 0$ °C per hr. The crystal thus obtained for neutron work weighed about 420 mg.

As the accurate determination of the lattice parameters was impossible with this crystal because of its bulkiness,

X-ray photographs were taken with powders and also with much thinner crystals which were prepared in exactly the same way. These samples showed $4 \times a_0$ superlattice reflexions with $a_0 = 5 \cdot 441 \pm 0 \cdot 0005$ Å (Masaki, unpublished), which are the known characteristics of the U_4O_9 phase (Belbeoch, Piekarski & Perio, 1961; Belbeoch, Laredo & Perio, 1964). This indicated that the crystal prepared by the above-described procedures was really of the U_4O_9 phase.

In fact when X-ray Laue, oscillation and Weissenberg photographs of the 420 mg crystal were taken, it was found that all the observed reflexions including faint superlattice spots could be indexed on the basis of a single $4 \times a_0$ cubic lattice with $a_0 = 5 \cdot 44$ Å, and it was confirmed that the crystal used for the neutron diffraction work was of single phase and of composition close to U_4O_9.
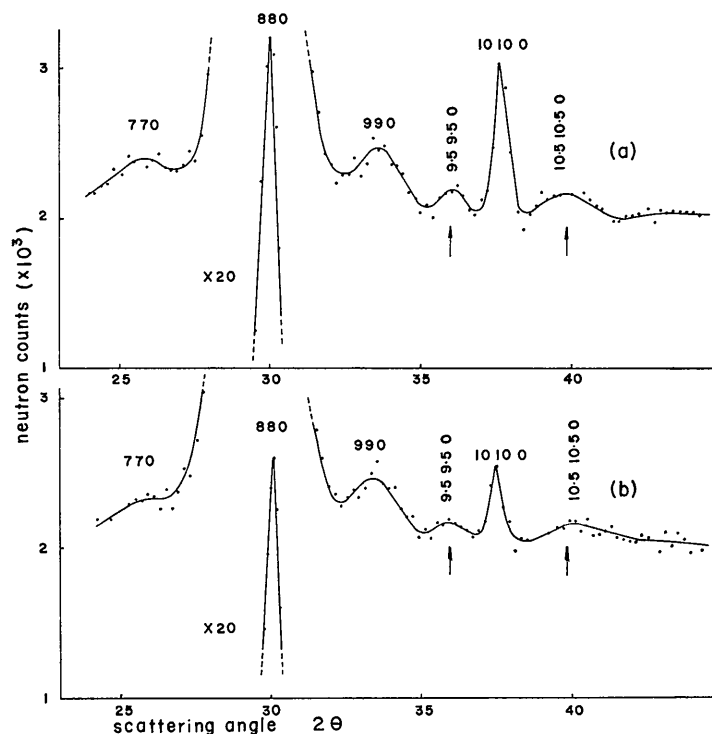

Fig. 1. A part of diffractometer records ranging along rekha [110], at (*a*) 120 °C and (*b*) 20 °C. Arrows indicate the $8 \times a_0$ superlattice reflexions. The ordinate scale for (880) fundamental is reduced to one-twentieth.

Neutron diffraction experiments were carried out by a diffractometer installed at the JRR-3 reactor of JAERI (10 MW, maximum thermal flux: 2×10^{13} n.cm^{-2}sec^{-1}), with a Cu (111) transmission-type monochromator which reflects 0·98 Å neutrons. The usual θ–2θ scanning was made along rekhas [110] and [1$\bar{1}$0], over 2θ ranging from 18° to 68°, at room temperature and at 120°C, *i.e.* below and above the transition point (75°C) which was observed and discussed by Naito, Ishii, Hamaguchi & Oshima (1967). Integrated intensities of the fundamental reflexions 880; 16,16,0, 800, 16,0,0, and 24,0,0 observed at room temperature agreed well with those given by Willis (1964) for U$_4$O$_9$ single crystal.

Fig. 1(a) and (b) reproduces parts of the diffractometer records along the [110] rekha, at room temperature and at 120°C, where the peaks are indexed on the basis of the $4 \times a_0$ superlattice. In both of the figures small but distinct peaks are seen in between adjacent $4 \times a_0$ superlattice peaks. Since they can be indexed by half-integers, the structure of U$_4$O$_9$ is very probably with the $8 \times a_0$ superlattice both above and below the transition point. This result is in contrast with the conclusion accepted at present, that there exists only a $4 \times a_0$ superlattice in the structure of U$_4$O$_9$

(Belbeoch, Piekarski & Perio, 1961). Another $8 \times a_0$ superstructure peak, *viz.* 14·5, 14·5, 0, is also observed on the [110] rekha. Similar extra peaks are seen on the [1$\bar{1}$0] diffractometer record as well, suggesting that the $8 \times a_0$ superlattice holds the cubic symmetry of the structure.

All of the observed $8 \times a_0$ superstructure reflexions showed the same behavior as most of the $4 \times a_0$ superstructure reflexions with respect to the phase transition (Naito *et al.*, 1967), *i.e.* their integrated intensities are stronger for the high-temperature phase than for the low-temperature phase.

Further analysis of the superstructure is in progress.

References

BELBEOCH, B., LAREDO, E. & PERIO, P. (1964). *J. Nuclear Mat.* **13**, 100.

BELBEOCH, B., PIEKARSKI, C. & PERIO, P. (1961). *Acta Cryst.* **14**, 837.

NAITO, K., ISHII, T., HAMAGUCHI, Y. & OSHIMA, K. (1967). *Solid State Comm.* **5**, 349.

WILLIS, B. T. M. (1964). *J. Physique*, **25**, 431.

# Unit cell and space group of 4,8-dichloro-2,6-diethylbenzo(1-2,4-5)bisoxazole.

By L. G. ROLDAN and M. H. LITT,* Allied Chemical Corporation, Central Research Laboratory, Morristown, New Jersey 07960, U.S.A.

The cell constants for 4,8-dichloro-2,6-diethylbenzo(1-2,4-5)bisoxazole are $a = 5·451 \pm 0·004$, $b = 13·398 \pm 0·006$, $c = 8·790 \pm 0·004$ Å; $\beta = 103·1 \pm 0·1°$. The crystals belong to the space group $P2_1/a$. There are two molecules per unit cell.

In the course of the investigation of the synthesis of some dichlorobisoxazoles the 2,6-diethyl substituted compound was prepared. Details of its synthesis and postulated molecular structure have been published (Litt & Idelson, 1966).

The unit cell and space group have been found to be consistent with the postulated structure:
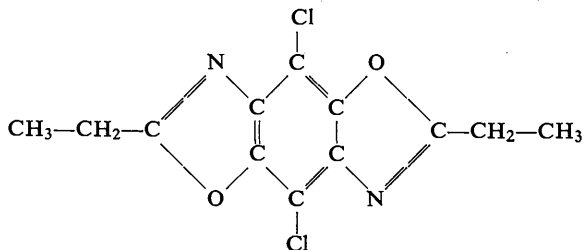
Single crystals were grown by recrystallization from benzene. They were found to be monoclinic and platelike, bounded principally by {110}. The cell constants determined from the zero layer of rotating crystal photographs

about the a and c axes with Cu $K\alpha$ radiation were refined by Bradley & Jay's (1932) extrapolation method. They are:

$$a = 5·451 \pm 0·004, \quad b = 13·398 \pm 0·006, \quad c = 8·790 \pm 0·004 \text{ Å};$$
$$\beta = 103·1 \pm 0·1°.$$

The calculated density based on two molecules per unit cell is 1·545 g.cm^{-3}, which is in agreement with an observed density of 1·55 g.cm^{-3}. Precession photographs about the c axis and the rotation photographs showed the $h0l$ reflections to be absent when $h = 2n + 1$ and the $0k0$ reflections to be absent when $k = 2n + 1$; there were no other systematic extinctions; the space group was thereby established as $P2_1/a$. Since this space group shows four general positions in the unit cell, each molecule must lie with its center on a center of symmetry.

It may be noticed that a disordered structure with respect to N and O is possible because of the nearly equal electron density of these atoms and the symmetrical positions of the two heavier chlorine atoms.

No further work on this compound is planned.

* Present address: Division of Polymer Science, Case Western Reserve University, University Circle, Cleveland, Ohio 44106, U.S.A.

References

BRADLEY, A. J. & JAY, A. H. (1932). *Proc. Phys. Soc.* **44**, 563.

LITT, M. H. & IDELSON, A. (1966). U.S. Patent 3,268,545.