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U$_4$O$_9$: atoms in general sites giving the *hkl* extinctions of special sites

N. C. Popa[a,b] and B. T. M. Willis[c]*

[a]Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research,141980 Dubna, Moscow Region, Russia, [b]National Institute for Materials Physics, PO Box MG-7, Bucharest, Romania, and [c]Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, England. Correspondence e-mail: bertram.willis@chem.ox.ac.uk

In U$_4$O$_9$, most of the atoms are in general 48-fold [48(e)] sites of the space group $I\bar{4}3d$ and yet the *hkl* reflections obey the extinction rules for atoms occupying special 12-fold [12(b)] sites. An explanation is given for this effect, which can be generalized to any space group.

1. Introduction

The crystal structure of the β phase of U$_4$O$_9$, which is stable above 353 K, was determined by Bevan *et al.* (1986) from the analysis of single-crystal neutron-diffraction data. They showed that most of the atoms in the unit cell occupy general 48-fold [48(e)] sites of the $I\bar{4}3d$ space group. Nevertheless, experiments using X-ray, neutron and electron diffraction have all confirmed that the *hkl* reflections conform to the reflection conditions of the special 12-fold [12(b)] sites. How is it possible for most of the atoms to occupy general positions and yet to give systematic *hkl* absences corresponding to special positions? In the following section, we shall show that the answer to this question is that the structure consists of several types of atomic clusters that are centred on the special sites. The cluster associated with each type must possess just one kind of atom, have the point-group symmetry of the crystal, and have the same orientation on being translated between equivalent positions of the special site. Before proceeding to detailed calculations, we shall summarize the extensive data on the symmetry of the diffraction pattern of U$_4$O$_9$.

Belbeoch *et al.* (1961) studied U$_4$O$_9$ using single-crystal and powder X-ray diffraction. They found that all the observed reflections, which covered an intensity range from 1 to 2500, obeyed the extinction rules of the 12(b) positions of the $I\bar{4}3d$ space group. On account of these rules, they stated that the structure consists of a 'unique motif' placed around the 12(b) sites and that this motif preserves the same orientation wherever it is applied. We shall use a similar concept in the treatment below.

Single crystals of U$_4$O$_9$ in the form of thin foils were examined by Blank & Ronchi (1968) employing electron diffraction. The diffraction pattern revealed numerous superlattice reflections including some not found by X-rays, especially at small angles of scattering. The conditions for possible reflections corresponded to the space group $I\bar{4}3d$, and all the superlattice extinctions were those associated with the subgroup 12(b).

Neutron diffraction studies of single crystals have been undertaken by Willis (1964), Masaki & Doi (1968), Bevan *et al.* (1986) and Lauriat *et al.* (1989). Masaki & Doi observed two weak reflections, 770 and 990, and so they re-assigned the space group as $I4_132$. The other workers failed to confirm the existence of these weak reflections, and they all agreed with Perio's assignment of $I\bar{4}3d$. Lauriat *et al.* (1989) stated: 'We find that superlattice reflections whose indices are h, k, l = $8n \pm 1$, $8n \pm 1$, $4n$ and $8n \pm 3$, $8n \pm 3$, $4n$ are unobservable without exception. These indices correspond to the extinction rules of the 12(a), 12(b) positions of the $I\bar{4}3d$ space group.' Bevan *et al.* (1986) found that these extinction rules are obeyed at a temperature of 503 K, but Cooper & Willis (2004) found that they break down at 773 K. We shall proceed on the assumption that the reflections obey the 12(b) extinction rules of $I\bar{4}3d$ at low temperatures.

The complete set of rules for 12(b) [or 12(a)] is given in Table 1, where N denotes an integer. *They imply that approximately one in four of the reflections that are expected for atoms occupying 48(e) Wyckoff sites are, in fact, forbidden.*

2. Diffraction from atomic clusters centred on 12(b) sites

Consider the case of a crystal with space group $I\bar{4}3d$ in which all the atoms are of the same type and occupy general 48(e) positions. The number of atoms in the unit cell is a multiple of 48, so that there are 48n atoms, $n \geq 1$. They can be divided into two groups, each of 24n atoms, which are related by a translation with the lattice vector $\mathbf{C} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (body centring). The diffraction amplitude of the unit cell is then

Table 1
12(*b*) extinction rules.

	h	*k*	*l*
h, *k*, *l* = even, even, even *allowed*	4*N*+2	4*N*+2	4*N*
	4*N*+2	8*N*+4	4*N*
	4*N*	4*N*	4*N*
h, *k*, *l* = even, even, even *disallowed*	4*N*+2	4*N*+2	4*N*+2
	4*N*+2	8*N*	8*N*
	4*N*+2	8*N*+4	8*N*+4
h, *k*, *l* = odd, odd, even *allowed*	2*N*+1	2*N*+1	4*N*+2
	8*N*+1	8*N*+3	4*N*
	8*N*+1	8*N*+5	4*N*
	8*N*+3	8*N*+7	4*N*
	8*N*+5	8*N*+7	4*N*
h, *k*, *l* = odd, odd, even *disallowed*	8*N*+1	8*N*+1	4*N*
	8*N*+1	8*N*+7	4*N*
	8*N*+3	8*N*+3	4*N*
	8*N*+3	8*N*+5	4*N*
	8*N*+5	8*N*+5	4*N*
	8*N*+7	8*N*+7	4*N*

$F(hkl)$

$$= f \sum_{m=1}^{24n} \exp(-W_m)\{\exp(2\pi i\mathbf{H} \cdot \mathbf{r}_m) + \exp[2\pi i\mathbf{H} \cdot (\mathbf{r}_m + \mathbf{C})]\}$$

$$= f[1 + \cos \pi(h + k + l)] \sum_{m=1}^{24n} \exp(-W_m)[\exp(2\pi i\mathbf{H} \cdot \mathbf{r}_m)],$$
$$(1)$$

where f is the (X-ray, neutron, electron) scattering amplitude for a spherical atom, $\mathbf{H}(hkl)$ is the reciprocal-lattice vector, $\mathbf{r}_m$ is the position vector of the atom m and $\exp(-W_m)$ is the Debye–Waller temperature factor, which may be anisotropic. If we apply (1) to the special site 12(*b*), we need to take into account only the six Wyckoff sites

$$(\tfrac{7}{8}, 0, \tfrac{1}{4}), (\tfrac{1}{4}, \tfrac{7}{8}, 0), (0, \tfrac{1}{4}, \tfrac{7}{8}), (\tfrac{5}{8}, 0, \tfrac{3}{4}), (\tfrac{3}{4}, \tfrac{5}{8}, 0), (0, \tfrac{3}{4}, \tfrac{5}{8}) \quad (2)$$

because the remaining six 12(*b*) sites are related to those in (2) by the lattice vector $\mathbf{C}$.

The point symmetry of a 12(*b*) site is $\bar{4}$. If we start from a single atom in a general xyz position, giving this atom the coordinates (a, b, c) with respect to the site $(\tfrac{7}{8}, 0, \tfrac{1}{4})$ chosen as origin of coordinates, we shall have a total of four atoms in a cluster of $\bar{4}$ symmetry surrounding this site. These atoms will have the coordinates (a, b, c), $(a, -b, -c)$, $(-a, c, -b)$ and $(-a, -c, b)$. The other 20 symmetry-related general positions will yield similar four-atom clusters around the other five 12(*b*) sites in (2). Three of the four-atom clusters will be the same, but oriented along the three cell-axis directions (effect of threefold axes); the other three will be related *via* diagonal mirrors. Since we started with 24 atoms in general positions, there are no *hkl* selection-rule simplifications. We shall show, however, that the 12(*b*) selection-rule simplification arises if a copy of the atom with coordinates (a, b, c) is placed at *each* of the six sites in (2), where the origin of coordinates for each copy is the site itself. This procedure generates a total of 24 × 6 or 144 atoms, consisting of 24-atom clusters at the six sites in the unit cell. The clusters are identical to one another

in geometry and orientation, have the point group $\bar{4}3m$, and are related by a translation vector that is not a lattice vector.

Although the 24-atom clusters around 12(*b*) sites are identical to one another, they are formed from non-equivalent atoms. Thus only four atoms in every cluster are equivalent and these atoms correspond to the axis $\bar{4}$ [the point group of the sites 12(*b*)]. The other 20 atoms are equivalent four-by-four with atoms from different clusters. For example, in the cluster centred on $(\tfrac{7}{8}, 0, \tfrac{1}{4})$, only the atoms (a, b, c), $(a, -b, -c)$, $(-a, c, -b)$ and $(-a, -c, b)$ are equivalent and they correspond to the axis $\bar{4}$ oriented along [100]. The atoms (b, c, a), $(b, -c, -a)$, $(-b, a, -c)$ and $(-b, -a, c)$ from the same cluster are not equivalent with the previous four, but with the atoms (a, b, c), $(-a, b, -c)$, $(c, -b, a)$ and $(-c, -b, a)$ from the cluster centred on $(\tfrac{1}{4}, \tfrac{7}{8}, 0)$, and so on. In other words, the clusters are identical and have the point-group symmetry $\bar{4}3m$, not because all atoms of the cluster are equivalent but because an identical atom (a copy) was placed at the point (a, b, c) around each 12(*b*) site. By applying to these atoms all operations of the space group, we obtain identical clusters in both geometry and orientation.

Let $\mathbf{R}_i$ be the position vector of the *i*th Wyckoff 12(*b*) site with respect to the origin of the unit cell and let $\mathbf{r}_{ij}$ be the position vector of the *j*th atom in the cluster S_i surrounding the *i*th site with respect to an origin at that site. The position vector in the unit cell of the atom j is $\mathbf{R}_i + \mathbf{r}_{ij}$ and, denoting by $\exp(-W_{ij})$ the corresponding Debye–Waller factor, in place of (1) we have:

$$F(hkl) = f[1 + \cos \pi(h + k + l)]$$
$$\times \sum_{i=1}^{6} \sum_{j=1}^{4n} \exp(-W_{ij}) \exp[2\pi i\mathbf{H} \cdot (\mathbf{R}_i + \mathbf{r}_{ij})]$$
$$= f[1 + \cos \pi(h + k + l)]$$
$$\times \sum_{i=1}^{6} \left[\exp(2\pi i\mathbf{H} \cdot \mathbf{R}_i) \sum_{j=1}^{4n} \exp(-W_{ij}) \exp(2\pi i\mathbf{H} \cdot \mathbf{r}_{ij}) \right].$$
$$(3)$$

Because the clusters are identical in both geometry and orientation, the quantities $\mathbf{r}_{ij}$, W_{ij} in the inner sum of (3) are the same for each cluster S_i and so they are independent of the index *i*. Hence,

$$\mathbf{r}_{ij} = \mathbf{r}_j \neq 0, \quad W_{ij} = W_j. \quad (4)$$

Equation (3) can then be factorized to yield the expression

$$F(hkl) = f[1 + \cos \pi(h + k + l)]$$
$$\times \left[\sum_{j=1}^{4n} \exp(-W_j) \exp(2\pi i\mathbf{H} \cdot \mathbf{r}_j) \right] \left[\sum_{i=1}^{6} \exp(2\pi i\mathbf{H} \cdot \mathbf{R}_i) \right].$$
$$(5)$$

The factor $\sum_{i=1}^{6} \exp(2\pi i\mathbf{H} \cdot \mathbf{R}_i)$ in (5) is the sum of the amplitudes of unit scatterers at the special positions 12(*b*), and follows the special selection rules for that site. On the other hand, there are no selection rules for the factor $\sum_{j=1}^{4n} \exp(-W_j) \exp(2\pi i\mathbf{H} \cdot \mathbf{r}_j)$ in (5).

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Hitherto, we have considered only one type of atom in the unit cell. For several types of atom (as in U_4O_9), there are different clusters for each type and equation (5) must be summed over each atomic species with the corresponding scattering factor and thermal parameters.

To determine the *xyz* coordinates of the atoms in the clusters surrounding the special sites in (2), we start with the six atoms in different clusters with local coordinates (a, b, c). For these atoms,

$$(xyz)_i = \mathbf{R}_i + (a, b, c) \in S_i = (x_i + a, y_i + b, z_i + c), \quad (6)$$

where (x_i, y_i, z_i) are the coordinates of the special sites. The expression $(a, b, c) \in S_i$ denotes the vector (a, b, c) translated to the centre of S_i as origin. The six atoms take the same exponent of the Debye–Waller factor:

$$\begin{aligned} W &= 2\pi^2 \langle (\mathbf{u} \cdot \mathbf{H})^2 \rangle \\ &= 2\pi^2 [\langle u_x^2 \rangle h^2 + \langle u_y^2 \rangle k^2 + \langle u_z^2 \rangle l^2 \\ &\quad + 2\langle u_x u_y \rangle hk + 2\langle u_y u_z \rangle kl + 2\langle u_x u_z \rangle hl]. \end{aligned} \quad (7)$$

Here the symbol $\langle ... \rangle$ represents the average value and $\mathbf{u} = (u_x, u_y, u_z)$ is the atomic displacement vector due to thermal vibrations.

For each atom in (6), there exists another 23 equivalent atoms spread across the unit cell. Their coordinates are calculated as follows. The general equivalent positions of the space group $I\bar{4}3d$ are

$$x, y, z; \tfrac{1}{2} + x, \tfrac{1}{2} - y, -z; -x, \tfrac{1}{2} + y, \tfrac{1}{2} - z; \tfrac{1}{2} - x, -y, \tfrac{1}{2} + z; \ldots \quad (8)$$

and, as an example, we take the general position $(\tfrac{1}{2} + y, \tfrac{1}{2} - z, -x)$ operating on the atom at (a, b, c) in the first cluster S_1, centred on $(\tfrac{7}{8}, 0, \tfrac{1}{4})$. From (6), we have

$$x = \tfrac{7}{8} + a, \quad y = b, \quad z = \tfrac{1}{4} + c$$

and the unit-cell coordinates of the transposed atom are

$$\begin{aligned} (\tfrac{1}{2} + y, \tfrac{1}{2} - z, -x)_1 &= (\tfrac{1}{2} + b, \tfrac{1}{4} - c, \tfrac{1}{8} - a) \\ &= (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) + (b, \tfrac{3}{4} - c, \tfrac{5}{8} - a), \quad (9a) \end{aligned}$$

where the subscript on the left-hand side refers to the first cluster, S_1. The sixth special site in (2) is at $(0, \tfrac{3}{4}, \tfrac{5}{8})$ and so $(\tfrac{1}{2} + y, \tfrac{1}{2} - z, -x)_1 = \mathbf{R}_6 + (b, -c, -a) \in S_6$.

Similarly, for the atom at (a, b, c) in the third cluster S_3, centred on $(0, \tfrac{1}{4}, \tfrac{7}{8})$, $x = a$, $y = \tfrac{1}{4} + b$, $z = \tfrac{7}{8} + c$. The general equivalent position $(-y, \tfrac{1}{2} + z, \tfrac{1}{2} - x)$ operating on this atom gives the coordinates

$$\begin{aligned} (-y, \tfrac{1}{2} + z, \tfrac{1}{2} - x)_3 &= (-\tfrac{1}{4} - b, \tfrac{3}{8} + c, \tfrac{1}{2} - a) \\ &= (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) + (\tfrac{1}{4} - b, \tfrac{7}{8} + c, -a) \\ &= \mathbf{R}_2 + (-b, c, -a) \in S_2. \quad (9b) \end{aligned}$$

By proceeding systematically in this way, we can calculate all the atomic positions of (6). n in equation (5) is equal to 6, and the complete set of coordinates is then given by expressions such as (9a), (9b) with the following permutations of (a, b, c):

$$\begin{aligned} &(a, b, c), (a, -b, -c), (-a, b, -c), (-a, -b, c); \\ &(b, c, a), (b, -c, -a), (-b, c, -a), (-b, -c, a); \\ &(c, a, b), (c, -a, -b), (-c, a, -b), (-c, -a, b); \\ &(a, c, b), (a, -c, -b), (-a, c, -b), (-a, -c, b); \\ &(c, b, a), (c, -b, -a), (-c, b, -a), (-c, -b, a); \\ &(b, a, c), (b, -a, -c), (-b, a, -c), (-b, -a, c). \end{aligned} \quad (10)$$

This set of 24 values describes a *hexatetrahedral* cluster of 24 atoms centred on every $12(b)$ site. The cluster has the point symmetry $\bar{4}3m$, which is the point symmetry of the space group $I\bar{4}3d$. The coordinates in (10) are those of the general positions of the primitive symmorphic group $P\bar{4}3m$

For $a \neq b \neq c \neq 0$, there are $24 \times 6 \times 2 = 288$ atoms in the unit cell (including the body centring condition) but there are fewer atoms [*i.e.* $n < 6$ in equation (5)] if constraints are imposed on a, b, c. For $b = c \neq a$, there are 12 atoms in the cluster (144 in the unit cell); for $a \neq 0$ and $b = c = 0$, there are six atoms (*octahedral* grouping); for $a = b = c$, there are only four atoms (*tetrahedral* grouping); and, for $a = b = -c$, there are similarly four atoms (*inverse tetrahedral* grouping). In these particular cases, the atoms in the cluster sit in special positions of the space group $P\bar{4}3m$. Thus, in the *tetrahedral* cluster, the atoms sit in the special position $3m$ of $P\bar{4}3m$ and the multiplicity is that of the point group $\bar{4}$. Clearly, there is the possibility of accommodating many different clusters for a given type of atom by taking different sets of (a, b, c) and also by using the second special position $12(a)$. We shall see in the subsequent paper that clusters with tetrahedral, octahedral and hexatetrahedral symmetry all exist in U_4O_9.

It is an easy matter to find the Debye–Waller factors of the 24 atoms in (10). Indeed, the equivalents of the thermal displacement vector $\mathbf{u}$ are just those given by (10), changing only (a, b, c) into (u_x, u_y, u_z). Thus, for example, we have for the tenth atom in the list of coordinates in (10):

$$\begin{aligned} W_{10} &= 2\pi^2 [\langle u_y^2 \rangle h^2 + \langle u_z^2 \rangle k^2 + \langle u_x^2 \rangle l^2 \\ &\quad - 2\langle u_y u_z \rangle hk + 2\langle u_x u_z \rangle kl - 2\langle u_x u_y \rangle hl]. \end{aligned}$$

3. Generalization to any space group

The treatment presented in the previous section can be generalized to any space group if the atoms occupy a general position but the diffraction pattern shows selection rules for a special position. Let us denote by n_g the number of general equivalent sites, by n_s the number of special equivalent sites, both without counting the lattice condition of face or body centring, and by n_c the number of vectors $\mathbf{C}_m$ giving the lattice centring ($n_c = 1$, 2 or 4, and $n_c = 3$ for the rhombohedrally centred hexagonal lattice).

We start by placing one atom close to each of the n_s sites. This atom is in a general position given by $(xyz)_i = \mathbf{R}_i + (a, b, c) \in S_i$ ($i = 1, n_g$).

(a, b, c) is an arbitrary vector $\mathbf{r}_1$ referred to an origin at the ith special site. The n_g equivalents of every one of these atoms

are spread across all n_s subgroups $S_1, \ldots, S_{n_s}$, with n_g/n_s atoms in every subgroup. Thus there are n_s identical clusters, each containing n_g atoms centred on a special site. These clusters have the point-group symmetry of the space group and are related to one another by translation only. The coordinates and the Debye–Waller factors of all atoms from these clusters are then

$$(xyz)_{ij} = \mathbf{R}_i + \mathbf{r}_j \in S_i; \quad W_{ij} = W_j = 2\pi^2 \langle (\mathbf{u}_j \cdot \mathbf{H}) \rangle^2$$
$$(i = 1, n_s; \; j = 1, n_g),$$

where $\mathbf{r}_j = \mathbf{r}_1 \cdot \Phi_j$ and $\mathbf{u}_j = \mathbf{u}_1 \cdot \Phi_j$. Here Φ_j is an operation of the point group.

In practice, we need not calculate $\mathbf{r}_j$ and $\mathbf{u}_j$ because they are listed in *International Tables for X-ray Crystallography* (1969) as general positions of the corresponding primitive symmorphic space group, having the same point group as the actual space group. Including the lattice centring, the number of atoms in the unit cell for one set of a, b, c is $n_c \times n_g \times n_s$ and the diffraction amplitude can be written as follows:

$$F(hkl) = f \left[\sum_{m=1}^{n_c} \exp(2\pi i \mathbf{H} \cdot \mathbf{C}_m) \right] \left[\sum_{j=1}^{n_g} \exp(-W_j) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) \right]$$
$$\times \left[\sum_{i=1}^{n_s} \exp(2\pi i \mathbf{H} \cdot \mathbf{R}_i) \right]. \tag{11}$$

The terms within the first square brackets in (11) represent the amplitude due to the centring. The second square brackets contain the amplitude of the cluster, which has no selection rules. The terms in the last square brackets contain the sum of amplitudes of the special sites, which (together with the terms in the first parentheses) follow the selection rules of these sites, although the atoms sit in general positions. For more than one type of atom in the unit cell, equation (11) must be summed over the different atomic species with corresponding scattering factors and thermal parameters.

4. Conclusions

We have shown that the reflection conditions of a special Wyckoff site are unchanged when a single atom occupying that site is replaced by a cluster of the same type of atom which possesses the point-group symmetry of the space group. It is also necessary that the clusters at the equivalent positions of the special sites are related by pure translation operators.

More generally, if the point-group symmetry of the cluster is equal to the point-group symmetry of the space group or a supergroup of this space group, then the reflection conditions are identical to those found when a single spherical unit is placed exactly at the special position. These statements are generalizations of the comment in *International Tables for X-ray Crystallography* (1969): 'It should be remembered that the special conditions only apply when the special positions are assumed to be occupied by spherical groups.' The related topic of the diffraction enhancement of symmetry has been treated by Iwasaki *et al.* (see Perez-Mato & Iglesias, 1977), in which the point-group symmetry of the diffraction pattern is *higher* than the point-group symmetry of the crystal. This treatment does not apply to the present case where the two symmetries are the same.

In the structure of U_4O_9 described by Bevan *et al.* (1986), it was found that the unit cell contains clusters of atoms centred on the $12(b)$ sites. Each cluster possesses point-group symmetry $\bar{4}3m$ and contains just one kind of atom, U or O. Most of the atoms were allocated to 15 general xyz sites but the data were too few to allow refinement of these 45 positional parameters individually. Using the present analysis, the number of independent parameters is substantially reduced, and in the following paper we shall describe the refinement of neutron diffraction data for U_4O_9, taking into account the special extinction rules for $12(b)$ sites.

References

Belbeoch, B., Piekarski, C. & Perio, P. (1961). *Acta Cryst.* **14**, 837–843.
Bevan, D. J. M., Grey, I. E. & Willis, B. T. M. (1986). *J. Solid State Chem.* **61**, 1–7.
Blank, H. & Ronchi, C. (1968). *Acta Cryst.* A**24**, 657–666.
Cooper, R. I. & Willis, B. T. M. (2004). *Acta Cryst.* A**60**, 322–325.
International Tables for X-ray Crystallography (1969). Vol. I. Birmingham: Kynoch Press.
Lauriat, J. P., Chevrier, G. & Boucherle, J. X. (1989) *J. Solid State Chem.* **80**, 80–93.
Masaki, N. & Doi, K. (1968). *Acta Cryst.* B**24**, 1393–1394.
Perez-Mato, J. M. & Iglesias, J. E. (1977). *Acta Cryst.* A**33**, 466–474.
Willis, B. T. M. (1964). *J. Phys.* **25**, 431–439.