which uses two parameters cannot produce a significant improvement over the result using model II. This assertion is made assuming that model IV will be the appropriate unconstrained model. From Table 3 we have

$$\mathscr{R}^{\text{obs}}(\text{II/IV}) = 1{\cdot}005$$

which corresponds to a significant improvement only if $N_{\text{unc}} - N_c = 1$, (see Table 3, *cf.* entry for II/III).

Conclusion

The molecules of S_8 are significantly distorted in the crystal, but no attempt is made yet to interpret the distortion. We plan to use the free molecule force field of Cyvin and our own crystal potential model to calculate both the distortion and the change in the internal mode frequencies and eigenvectors. By this time more accurate X-ray and neutron data may be available for analysis, as measurements are currently in progress under the direction of Professor P. Coppens (X-rays) and Dr Krebs Larsen (neutrons).

The rigid-body motion model is shown to fit the data very well, but it is made clear that on no account can one make the deduction that the molecules behave as rigid bodies. This result is so forceful because of the high symmetry of the S_8 molecule, so the reader is left to wonder just how important is the effect of the internal modes on the values of **T**, **L**, and **S** in other cases.

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The Structure of α-UO_3 by Neutron and Electron Diffraction

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The structure of α-UO_3 has been re-examined by neutron and electron diffraction. Analysis of the intensity of the neutron Bragg reflexions indicates that $12 \pm 1\%$ of the uranium sites are vacant in a disordered manner and that neighbouring U–O distances along the uranium–oxygen chains are shortened to $1{\cdot}64 \pm 0{\cdot}04$ Å. The earlier descriptions of the structure are inadequate and it is shown that the average sub-cell contents are similar to those expected for uranium deficient α-U_3O_8. The results explain earlier density and infrared observations. The superlattice reflexions observed in both neutron and electron diffraction patterns can be indexed on an orthorhombic unit cell with dimensions $a_o = 6{\cdot}84$, $b_o = 43{\cdot}45$, $c_o = 4{\cdot}157$ Å. There is a strong resemblance between the structures of α-UO_3 and *L*-Ta_2O_5.

Introduction

α-UO_3 is regarded as a basic structure type simply related to other well known structures (Hyde, 1971). In particular α-U_3O_8 is usually described as oxygen deficient α-UO_3 with ordered oxygen vacancies. However there is evidence to suggest that the presently accepted structure is too simple and needs reconsideration. The present paper, therefore, examines the structure of α-UO_3 in the light of new electron and neutron diffraction data.

An early X-ray diffraction study by Zachariasen (1948) suggested a trigonal structure for α-UO_3 ($P\bar{3}m1$, $a = 3{\cdot}971$; $c = 4{\cdot}17$ Å) with one UO_3 molecule per unit cell as shown in Fig. 1. This model however fails to account for the powder neutron diffraction data of Loopstra & Cordfunke (1966) (the minimum R value obtained was 0·35 even after readjustment of the oxygen positions) so that they proposed the orthorhombic unit cell ($C2mm$, $a = 3{\cdot}961$; $b = 6{\cdot}860$; $c = 4{\cdot}166$ Å) shown in Fig. 2. It can be seen that the two structures are similar; in both there are linear

O–U–O–U–O chains with the uranium surrounded by six additional oxygen atoms lying approximately in a plane normal to the chains. There are three points nevertheless which should be noted about the Loopstra & Cordfunke investigation: (*a*) the R value is still high at 0·19; (*b*) the orthorhombic structure should give rise to splitting of the Bragg reflexions: that they are not observed is due to mimetic twinning; and (*c*) some additional though ill-defined reflexions suggest that the true unit cell may be a multiple of the proposed orthorhombic 'sub-cell'.

The main doubts emerge however because neither of these structures can explain the abnormally low density or the infrared absorption spectrum. There have been three experimental determinations of the density of α-UO_3: 7·04 g.cm^{-3} (Hoekstra & Siegel, 1961), 7·25 g.cm^{-3} (Loopstra & Cordfunke, 1966) and 7·30 g.cm^{-3} (Siegel & Hoekstra, 1971), all much lower than the value of 8·39 g.cm^{-3} calculated from the lattice parameters quoted by the latter authors. Strong infrared absorption occurs around 930 cm^{-1} (Hoekstra & Siegel, 1961; Carnall, Walker & Neufeldt, 1966) which is characteristic of the asymmetric stretching vibration (ν_3) of the uranyl (UO_2^{2+}) cation and is therefore indicative of a U–O bond distance of approximately 1·7 Å (Jones, 1959). In fact isolated UO_2^{2+} cations do not exist in either the Zachariasen or the Loopstra & Cordfunke model and it seems unreasonable to attribute the absorption to a stretching vibration of the linear chains in which the U–O distance is 2·08 Å. The apparent complexity of the structure α-UO_3 has recently been commented on by Siegel & Hoekstra (1971).

Experimental

α-UO_3 was prepared by heating uranyl peroxide $UO_4.2H_2O$ at 470°C for 8 hours (Cordfunke, 1961) and analysed by reduction to U_3O_8 in air at 800°C. A stoichiometry of $UO_{3\cdot03\pm0\cdot03}$ was indicated. The Debye–Scherrer X-ray reflexions could be indexed on a hexagonal unit cell with lattice parameters ($a = 3\cdot950 \pm 0\cdot004$; $c = 4\cdot157 \pm 0\cdot003$ Å) slightly smaller than those previously observed (see Introduction).

Neutron diffraction measurements were carried out on the powder diffractometer PANDA at A.E.R.E. Harwell. The sample was contained in a thin-walled vanadium can and examined with neutrons ($\lambda = 1\cdot522$) obtained by reflexion from the (331) planes of a germanium monochromator with a take-off angle of 72°. Two electron microscopes were used: a JEM 6A and a JEM 100U both operated at 100 kV. Crystals of the sample were supported by a carbon film deposited on a copper grid.

Results

Neutron diffraction

The neutron diffraction pattern shows the main hexagonal sub-cell reflexions and in addition a number of weak and rather poorly defined superlattice peaks. The first twelve fundamental reflexions could be used to determine the average content of the sub-cell but beyond Q ($=4\pi \sin \theta/\lambda) = 5\cdot3$ Å^{-1} the peaks were too broad and overlapped too extensively for accurate estimates of intensity. The measured intensities are in close agreement with those calculated from the data of Loopstra & Cordfunke and both sets of measurements have been used in the subsequent analysis. As expected the present results do not fit the Zachariasen model but the orthorhombic model gives a slightly improved result. The atom positions for trial structures were refined using scattering lengths of $b_O = 0\cdot577 \times 10^{-12}$ cm. (The Neutron Diffraction Commission, 1969) and $b_U = 0\cdot850 \times 10^{-12}$ cm (Willis, 1963; Atoji, 1966) using a least-squares program written by P. J. Wiseman. The program minimizes the function $w_i[I_{\rm obs} - I_{\rm calc}]^2$ where the weighting factor $w_i = 1/\sigma^2$. In the orthorhombic structure the x and y coordinates of the oxygen atoms in the (001) plane were refined along with the temperature factors (assumed isotropic) for uranium and oxygen. The values obtained are $x = 0\cdot16 \pm 0\cdot04$, $y =$

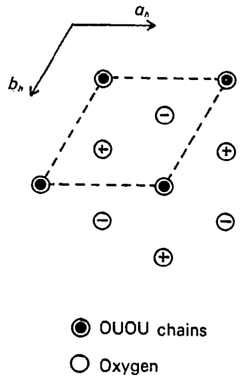

Fig. 1. The Zachariasen structure of α-UO_3 projected on to the (001) plane. The equatorial oxygen atoms lie above and below the plane, as indicated, with $z = \pm 0\cdot17$.

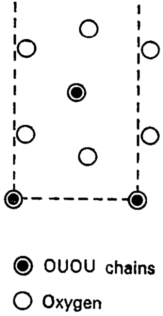

Fig. 2. The orthorhombic α-UO_3 unit cell of Loopstra & Cordfunke projected on to the (001) plane. The equatorial oxygen atoms lie in this plane.

$0{\cdot}33 \pm 0{\cdot}02$, $B_U = 3{\cdot}5 \pm 2{\cdot}5$ Å^2, $B_O = 3{\cdot}0 \pm 2{\cdot}3$ Å^2, $R(I) = 0{\cdot}19$. The inadequacy of this description is reflected in the high R index and in the high and imprecise temperature factors. The nearest O–O distances are short – approximately 2·28 Å – but it should be noted they are the maximum possible if a structure containing six coplanar oxygen atoms around a central uranium atom is to be retained.

The density measurements suggest the possibility that the uranium and oxygen sublattices are incomplete. Using the unit-cell parameters obtained in the present study the calculated density is 8·46 g.cm^{-3} which implies a vacancy concentration of 14% if the densities of Loopstra & Cordfunke and Siegel & Hoekstra are used or 17% based on the earlier Hoekstra & Siegel determination. The abnormally short inter-oxygen distances can be avoided if oxygen atoms are removed from the (001) plane. Just such a situation exists in α-U_3O_8 where (relative to a fully occupied α-UO_3 lattice) the oxygen sublattice is 11% deficient. An idealized structure of α-U_3O_8 ($C222$, D_2^6) has been described by Andresen (1958) [Fig. 3(*a*)] but the actual unit cell appears to be reduced in symmetry to $C2mm$ (Loopstra, 1964, 1970) [Fig. 3(*b*)] perhaps to allow small displacements to minimize oxygen–oxygen interactions. In this case the minimum O–O distance is now about 2·58 Å.

A simple way of viewing the α-UO_3 structure is to regard it as uranium deficient α-U_3O_8 with uranium vacancies introduced so as to re-establish an O:U stoichiometry of 3:1 and a refinement was carried out on this basis. The unit-cell parameters were assumed to be $a = 6{\cdot}842$, $b = 11{\cdot}850$, $c = 4{\cdot}157$ Å, *i.e.* $a = \sqrt{3}a_h$, $b = 3a_h$, $c = c_h$ where the subscript h refers to the hexagonal axes illustrated in Fig. 1. For the $C222$ space group there are too many variables to allow them all to vary independently. In order to reduce the number of adjustable parameters several assumptions were made: (i) the temperature factors B_U and B_O were fixed at reasonable values of 0·3 and 0·9 Å^2 respectively, (ii) oxygen atoms are removed only from the (001) plane and all the equatorial oxygen atoms are confined to this plane, (iii) uranium vacancies are present randomly and for each missing uranium atom there are two displaced oxygen atoms in the z direction. The independent variables thus reduce to a uranium (or oxygen) occupation number together with four oxygen positional parameters (see Table 1).

The success of the refinement (see Table 2) is striking with the R (intensity) index falling to 0·031, after four cycles. The results from the refinement account for the anomalies. α-UO_3 is found to have 12 ± 1% uranium (and oxygen) vacancies which reduces the theoretical density to $7{\cdot}44 \pm 0{\cdot}09$ g.cm^{-3} in good agreement with the most recently reported experimental values. The presence of uranium vacancies also explains the infrared absorption. Since approximately a quarter of the oxygen atoms within the O–U–O–U–O chains are coordinated to *one* rather than two uranium atoms strong uranyl-like absorptions are to be expected. The appearance of a U–O distance in the z direction of $1{\cdot}64 \pm 0{\cdot}04$ is indicative of these singly coordinated oxygens and correlates well with the observed infrared stretching frequency of 930 cm^{-1}.

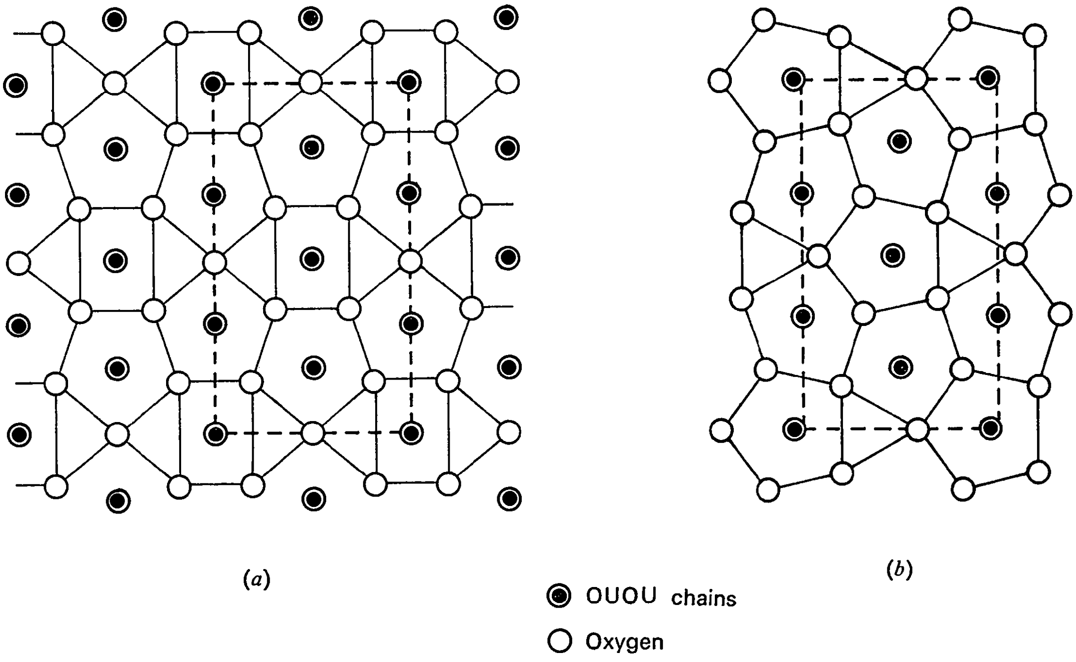

Fig. 3. The structures of α-U_3O_8 proposed by (*a*) Andresen & (*b*) Loopstra.

Table 1. *Atom positions in* α-UO_3 ($C222$)

The α-U_3O_8 atom positions of Andresen (1958) are shown in parentheses.

		x	y	z	B	P
U(1)	2(*a*)	0·0	0·0	0·0	0·3	0·878 ± 0·013
U(2)	4(*g*)	0·0	0·308 ± 0·001 (0·315)	0·0	0·3	1·756*
O(1)	4(*i*)	0·0	0·0	0·5	0·9	0·756*
O(2)	4(*h*)	0·0	0·308 ± 0·001 (0·315)	0·5	0·9	1·512*
O(3)	4(*i*)	0·0	0·0	0·395 ± 0·009	0·9	0·244*
O(4)	8(*l*)	0·0	0·308 ± 0·001 (0·315)	0·395 ± 0·009	0·9	0·488*
O(5)	2(*b*)	0·0	0·5	0·0	0·9	0·978*
O(6)	8(*l*)	0·168 ± 0·004 (0·19)	0·128 ± 0·001 (0·145)	0·0	0·9	3·913*

* All occupation parameters are dependent on $P_{U(1)}$, the value for U(1):

$P_{U(2)} = 2P_{U(1)}$

$P_{O(1)} = 1·0 - 2P_{U(1)}$

$P_{O(2)} = 2·0 - 4P_{U(1)}$

$P_{O(3)} = 2\ (1·0 - P_{U(1)})$

$P_{O(4)} = 4\ (1·0 - P_{U(1)})$

$P_{O(5)} = 1·0 - 1·8\ (0·889 - P_{U(1)})$

$P_{O(6)} = 4·0 - 7·2\ (0·889 - P_{U(1)})$

Table 2. *Calculated and observed intensities*

hkl	I_{calc}	I_{obs}	$\sigma(I_{\text{obs}})$	*hkl*	I_{calc}	I_{obs}	$\sigma(I_{\text{obs}})$
001	16·11	15·85	0·31	401 261	0·68	0·65	0·17
200 130	20·42	20·26	0·25	332 062	17·28	16·60	0·35
201 131	1·46	1·14	0·13	003	2·37	2·62	0·20
002	14·44	15·13	0·29	402 262	8·23	8·10	0·30
330 060	18·28	18·95	0·32	530 460 203 133 190	5·26	5·74	0·30
331 202 132 061	12·90	12·89	0·25				
400 260	7·79	7·52	0·22				

$R(I) = 0·031$†

† The Loopstra & Cordfunke (1966) data refined on the same basis give $R(I) = 0·058$.

The restrictions imposed by carrying out a refinement based on the Andresen structure may give rise to a somewhat idealized description of the α-UO_3 hexagonal sub-cell particularly when it is borne in mind that only certain oxygen displacements were allowed. In the light of a refinement carried out on the Loopstra $C2mm$ structure it does seem likely however that the basic subcell structure may have higher symmetry than in α-U_3O_8. In this refinement all the oxygen atoms were fixed in their α-U_3O_8 positions except for a proportion which could be displaced in the z direction because of the presence of uranium vacancies. The variables were now the uranium occupation number, one oxygen position and two temperature factors. Fairly reasonable values of the uranium occupation number and the U–O distance were obtained, (0·82 ± 0·04 and 1·58 ± 0·17 respectively), but the $R(I)$ value (0·13) and the uranium and oxygen temperature factors ($B_U = 0·7 \pm 0·9$, $B_O = 2·0 \pm 1·3$) were high.

Electron microscopy

The analysis of the fundamental reflexions of the hexagonal subcell has given a reasonable description of the basic α-UO_3 structure but the weak reflexions observed in the neutron diffraction pattern by both us and Loopstra & Cordfunke remain unexplained. The electron diffraction investigation also clearly shows superstructure reflexions in the (001) plane of the reciprocal lattice. The superlattice spots represented in Fig. 4(*a*) are typical of the majority of the crystals studied though patterns of the kind shown in Fig. 4(*b*) were also observed indicating that the sample had not quite reached equilibrium.

Accurate measurement of the reflexions in Fig. 4(*a*) lying along $[110]_h$ directions showed them to correspond to $\frac{9}{22}(110)_h$ and $\frac{13}{22}(110)_h$ and the spots can be indexed on an orthorhombic unit cell whose parameters a_o, b_o and c_o are related to those of the hexagonal sub-cell by $a_o = \sqrt{3}a_h$, $b_o = 11a_h$ and $c_o = c_h$ giving actual dimensions of $a_o = 6·84$, $b_o = 43·45$, $c_o = 4·157$ Å. The observed superstructure reflexions are 090, 0,13,0, 0,31,0, 120, 1,20,0 *etc.* and the two strongest extra peaks seen in the neutron difraction investigation are compatible with 060 and 090 reflexions. Orthorhombic pseudo-hexagonal structures of this type are commonly subject to mimetic twinning, the twin plane in this case being (1,11,0). Twinning of this kind would cause the appearance of superstructure reflexions in $[110]_h$, $[1\bar{2}0]_h$ and $[\bar{2}10]_h$ directions as observed.

The existence of micro-twins is supported by a dark-field microscopic investigation using a diffracted beam of the hexagonal subcell. The marked contrast effects which were observed were unlikely to have arisen from thickness variations and suggest considerable departure from a perfect single crystal.

Discussion

α-UO_3 clearly has an unusual structure in that in the stoichiometric compound there is a large concentration of disordered cation vacancies as well as ordered anion vacancies. Both cation and anion vacancies occur at the stoichiometric composition in certain metallic compounds such as TiO but in these compounds it is the creation of additional low lying electron energy levels which compensates for the expected endothermic enthalpy of defect formation. In α-UO_3 we can identify two factors which would encourage vacancy formation. One is the short O–O distances which follow if six oxygen atoms are placed around uranium in the (001) plane. Lowering the coordination in this plane from six to five effects considerable relaxation and presumably therefore a reduced repulsive energy. The second factor is the unusual strength of the uranyl bond which makes it plausible that the gain in energy associated with the contraction of some U–O distances from 2·1 to 1·6 Å to a considerable extent balances the loss in lattice energy associated with the removal of uranium atoms.

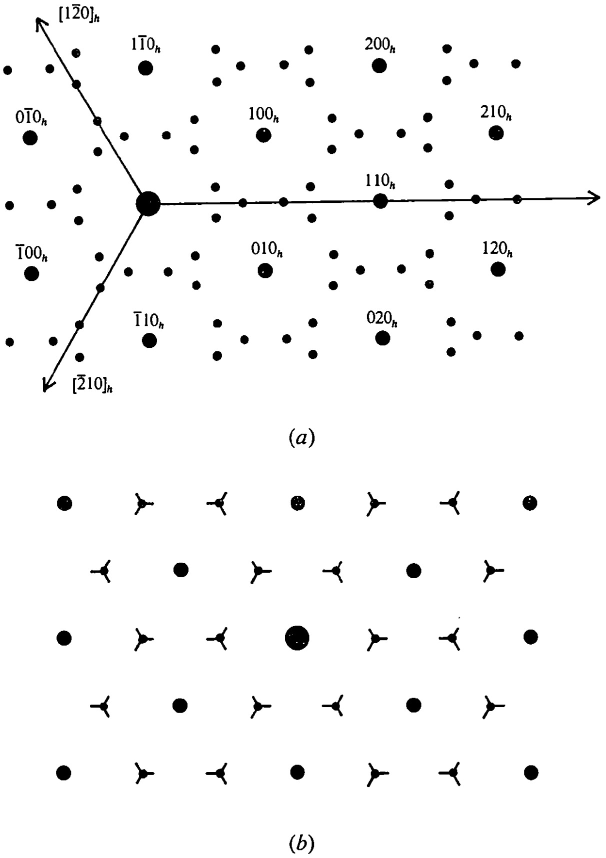

Fig. 4. (001) reciprocal lattice sections of α-UO_3 observed by electron diffraction.

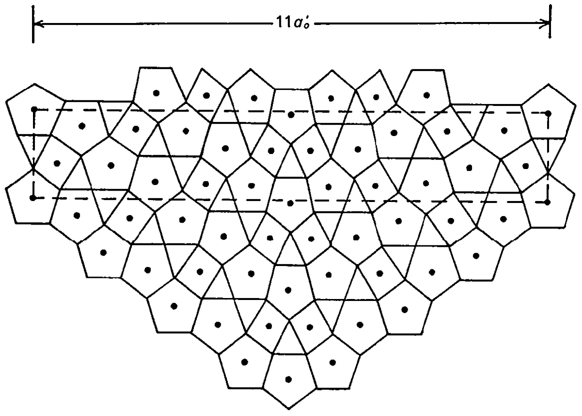

Fig. 5. A (001) projection of an idealized unit cell of L-Ta_2O_5.

The occurrence of a long period superlattice may be unexpected but it is not unknown in compounds with structures related to α-U_3O_8. The Andresen structure for α-U_3O_8 as we have seen in Fig. 3(*a*) consists of chains of edge-sharing pentagonal bipyramids which are attached to identical chains by corner sharing. Octahedral sites are produced between the chains. Roth & Stephenson (1969; see also Stephenson & Roth, 1971) have shown that these chains form the basis of structures in the Ta_2O_5–WO_3 system and that the oxygen:metal ratio can be reduced by folding the chains so that some octahedra share corners. A folded structure containing 11 orthorhombic cells of dimensions $a'_o=3\cdot663$; $b'_o=6\cdot198$; $c'_o=3\cdot888$ Å; (*cf.* original α-UO_3 structure of Loopstra & Cordfunke) corresponds to an ideal structure of L-Ta_2O_5 (Fig. 5) though the stoichiometry is $M_{22}O_{58}$. In the real structure of L-Ta_2O_5 Roth & Stephenson find evidence that some metal atoms undergo a reduction in coordination number from seven to six in distortion planes parallel to the x and z axes, and three such distortion planes reduce the contents of the unit cell to the required $M_{22}O_{55}$.

The superstructure reflexions observed by both electron and neutron diffraction in α-UO_3 are reminiscent of L-Ta_2O_5 for the extra reflexions can also be indexed on an enlarged unit cell containing 11 orthorhombic subcells. Furthermore we may note that in α-UO_3, some structural variation was observed between crystals, and similarly equilibrium was reached slowly in L-Ta_2O_5 (the structure containing 11 subcells was attained only after prolonged heating at 1350 °C). If, as seems highly likely, the two structures are analogous, then the two most probable structures for α-UO_3 are (*a*) an 11 sub-cell structure of nominal composition $U_{22}O_{58}$ but with 12·1% of the uranium sites vacant, *i.e.* $U_{19\cdot33}O_{58}$, or (*b*) an 11 sub-cell structure with one distortion plane per unit cell and 13·6% of the uranium sites vacant *i.e.* $U_{19}O_{57}$. The uranium occupation number is not determined accurately enough to distinguish between the two alternatives and this would require a single-crystal study. The powder measurements nevertheless allow us to conclude that the metal atom positions in α-UO_3 are somewhat different from those in L-Ta_2O_5. The X-ray superlattice reflexions in the latter compound arise predominantly from the metal displacements and the strongest reflexions predicted for the L-Ta_2O_5 structure are 080, 0,14,0, 0,30,0 *etc.* In α-UO_3 on the other hand the reflexions with observable intensity in the electron diffraction patterns are 090, 0,13,0, 0,31,0 *etc.* However, slight alteration in the y coordinates of some of the metal atoms is sufficient to effect this change in intensities. The neutron diffraction pattern for α-UO_3 was also calculated assuming the atom positions in L-Ta_2O_5 (except for the proportion of oxygen atoms displaced in the z direction because of the presence of uranium vacancies) but with occupation parameters modified to allow for the missing uranium atoms and in accordance with one distortion plane per unit cell. The correlation was rather poor $R(I)=0{\cdot}17$ but relaxation of uranium atoms in the [100] direction to correspond more closely to an ideal hexagonal arrangement reduced the R index to 0·09. A full refinement of such a large cell is impracticable from powder data but the indications from both the neutron and the electron diffraction experiments are that in α-UO_3 the position of the metal atoms approximate more closely to hexagonal symmetry than in L-Ta_2O_5.

We are grateful to the Science Research Council and A.E.R.E. Harwell for providing neutron diffraction facilities and one of us (CG) wishes to thank the S.R.C. for the provision of a studentship. We thank the University Support Group at A.E.R.E. Harwell for experimental assistance and P. J. Wiseman for the use of the computer program.

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The Crystal Structure of Hanksite, $KNa_{22}[Cl(CO_3)_2(SO_4)_9]$ and its Relation to the K_2SO_4 I Structure Type

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The crystal structure of hanksite, $KNa_{22}[Cl(CO_3)_2(SO_4)_9]$, has been determined by three-dimensional X-ray analysis and refined by least-squares methods, using anisotropic thermal parameters; final $R=0{\cdot}034$. The crystals are hexagonal ($P6_3/m$): $a=10{\cdot}490$, $c=21{\cdot}240$ Å, $Z=2$. The structure exhibits an ordered distribution of both SO_4 tetrahedra and CO_3 groups. The results of heating experiments are presented and similarities to a hexagonal phase of the solid solution series Ca_2SiO_4–$Ca_3(PO_4)_2$ with respect to the K_2SO_4 I structure type are discussed.

Introduction

The mineral hanksite, $KNa_{22}[Cl(CO_3)_2(SO_4)_9]$, belongs to the sulphates containing CO_3 groups. Ramsdall (1939) found hexagonal symmetry with the unit-cell dimensions $a=10{\cdot}46$ Å, $c=21{\cdot}18$ Å. $P6_3$ and $P6_3/m$ are proposed as possible space groups. A structure determination has, however, not been attempted. Furthermore Ramsdell (1939) found that the diffraction pattern of the high-temperature hexagonal Na_2SO_4–Na_2CO_3 series resembles the hanksite pattern. Additional reflexions indicate that the unit cell of hanksite has a c axis three times and an a axis twice the size of those of the Na_2SO_4–Na_2CO_3 series, or of Na_2SO_4 I. Eysel (1971) believes that hanksite is a variety of the hexagonal K_2SO_4 I structure type (high-