JOURNAL OF SOLID STATE CHEMISTRY **92**, 159–169 (1991)

Structure of the Insertion Compound $Li_{0.88}U_3O_8$ by Powder Neutron Diffraction

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Received April 12, 1990; in revised form December 21, 1990

The insertion compound $Li_{0.88}U_3O_8$, prepared from α-U_3O_8 at ambient temperature, was found to undergo an orthorhombic to hexagonal phase change on heating *in vacuo*. Powder neutron diffraction has been used to investigate the structures of the two modifications. Rietveld analysis of the data gave at, 573 K: space group $P\bar{6}2m$, $a = b = 6.849(3)$, $c = 4.197(1)$, and at, 295 K: space group $C2mm$, $a = 6.9107(8)$, $b = 11.7472(10)$, $c = 4.1919(4)$. In the stable high-temperature modification, lithium atoms occupy 5-coordinate, trigonal-bipyramidal sites located in an ordered array between layers of the α'-U_3O_8 structure.

Introduction

Conventional reprocessing of spent nuclear fuels involves oxidation of the fuel elements by heating in air, followed by dissolution in nitric acid (*1*). However, difficulty is encountered in oxidizing the uranium–plutonium mixed oxides used in fast-breeder reactors. Interest has been shown in using fused alkali-metal salts to digest spent fuels (*2*) by forming alkali-metal uranates. The lithium–uranium–oxygen system has been extensively studied in this connection (*3–5*). Compounds have been prepared by reaction of lithium carbonate or oxide with oxides of uranium, either in air, inert atmosphere, or *in vacuo*. The resulting phases fall into two broad groups, containing uranium in either the +6 or the +5 oxidation state. The former gives the more extensive series with Li : U ratios ranging from 1/3 to 6.

Both of these series of compounds have the characteristic property that the uranium is present in one formal oxidation state only. Recent work in this laboratory has led to the preparation and characterization of a range of lithium insertion compounds of the oxides of uranium (*6*). These compounds, of the general formula Li_xUO_n, contain uranium in more than one formal oxidation state. Controlling the extent of insertion, x, thereby enables the average oxidation state of the uranium to be varied. Insertion has been found to occur for α-, γ, δ-UO_3, and U_3O_8. Powder X-ray diffraction data demonstrate that insertion proceeds with minimal structural rearrangement.

In a recent paper we reported thermodynamic data on these insertion compounds (*7*). Measurements of the enthalpies of solution were used in conjunction with open-circuit voltage (OCV) measurements on suitable cells to derive thermodynamic quantities. In addition, enthalpies of decom-

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0022-4596/91 $3.00

TABLE I

LATTICE PARAMETERS OF $Li_xU_3O_8$-RELATED PHASES

	α-U_3O_8	$Li_{0.88}U_3O_8$[a] (295 K)	α'-U_3O_8[b]	$Li_{0.88}U_3O_8$[a] (573 K)
a	6.715	6.9107	6.812	6.849
b	11.968	11.7472	6.812	6.849
c	4.143	4.1919	4.142	4.197
α	90.0	90.00	90.0	90.0
β	90.0	90.0	90.0	90.0
γ	90.0	90.0	120.0	120.0

[a] From neutron study.

[b] After Ref. (*9*).

position to neighboring stable phases were calculated. Compounds of the form Li_xUO_3 were shown to be metastable, correlating with the observation that on heating δ-$Li_{0.69}UO_3$ *in vacuo*, a phase with a powder X-ray diffraction pattern resembling that of $LiUO_3$ is found among the products. However, the enthalpy of decomposition for the reaction:

$$Li_{0.88}U_3O_8 = 0.44\ Li_2U_3O_{10} + 0.12\ U_3O_8 + 1.32\ UO_2$$

was shown to be endothermic, indicating that $Li_{0.88}U_3O_8$ is probably a thermodynamically stable phase. In this paper, the thermal stability of this insertion compound is investigated and variable-temperature powder neutron diffraction is used to investigate the structures of the phases involved.

Experimental

$Li_xU_3O_8$ was prepared as previously reported (*6*) by reacting approximately 15 g of U_3O_8 with a large excess of anhydrous lithium iodide in dry carbon tetrachloride under an atmosphere of dry nitrogen. After stirring the mixture for 24 hr, the solid was washed with portions of carbon tetrachloride until the purple color of the liberated iodine was absent from the washings. The solid was further washed with portions of dry acetone, in order to remove any unreacted lithium iodide, and dried under vacuum. The flask was then removed to an argon dry box. The powder X-ray diffraction pattern of the resulting black solid was recorded and its composition determined by atomic absorption spectroscopy (AAS) and reducing-power analysis (*6*).

In order to investigate the thermal stability of the compound, a sample was sealed under vacuum into a silica tube. The inside of the tube was protected from possible attack by lithium by a coating of pyrolyzed graphite. The sample was heated at 300°C for a period of 5 days followed by cooling to room temperature within minutes. The experiment was repeated with the sample being cooled to room temperature over a period of a few hours. Powder X-ray diffraction patterns were recorded for the products. In addition, combined TGA/DTA traces for both $Li_{0.88}U_3O_8$ and α-U_3O_8 were recorded under an atmosphere of flowing nitrogen.

The powder neutron diffraction study was carried out on the Polaris spectrometer at ISIS. Approximately 10 g of $Li_{0.88}U_3O_8$ was loaded, under an atmosphere of dry argon, into an 8-mm diameter thin-walled vanadium can which was then sealed with a copper gasket. The can was mounted on a standard sample stick in a Leicester furnace fitted with a vanadium heating element and the furnace enclosure evacuated to a pressure of $<10^{-4}$ Torr. Data were collected at 295, 423, and 573 K. The data from individual detectors were focused using standard programs. These data sets were normalized by dividing by the incident spectrum derived from a previous run on vanadium powder in a vanadium can. The vanadium profile had been smoothed by the fitting of an empirical orthogonal polynomial and absorption and multiple scattering corrections were applied. Data manipulation and display was performed using the GENIE package on the RAL VAX.

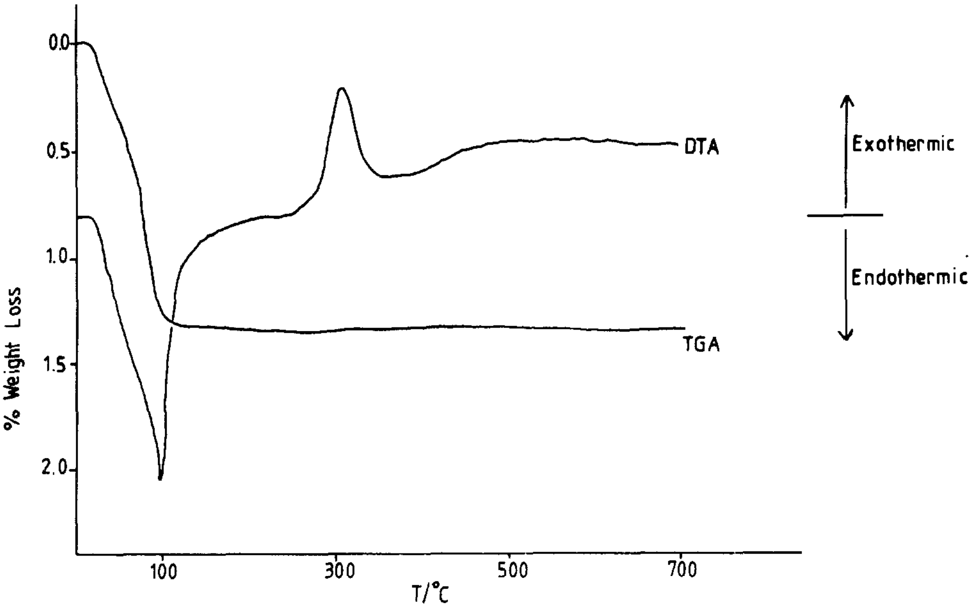

FIG. 1. TGA and DTA Traces for $Li_{0.88}U_3O_8$.

The reducing power of the sample was redetermined on removal from the sample can.

Results

Reducing-power and AAS analysis gave the mean composition as 0.88 ± 0.02. Powder X-ray diffraction data was in agreement with that reported previously and showed the compound to be a single phase indexable on an orthorhombic unit cell with lattice parameters which were slightly changed from those of the parent oxide. On heating $Li_{0.88}U_3O_8$ in a sealed tube the product gave an X-ray diffraction pattern which could be indexed on a hexagonal unit cell with cell parameters very close to those reported (*9*) for the high-temperature form of α-U_3O_8. The same product was found to result when the sample was quenched or underwent slow cooling. Table I summarizes the lattice parameters for these phases together with those of α- and α'-U_3O_8.

The DTA/TGA trace for $Li_{0.88}U_3O_8$ is given in Fig. 1. There are two features in the trace; first there is a small weight loss at a relatively low temperature (~80°C). This is accompanied by an endotherm. There is then an exotherm at higher temperature. For U_3O_8 no features were observed in either the DTA or TGA curves.

Redetermination of the reducing power of the sample after the neutron experiment confirmed that no loss of lithium had occured on heating. The profiles from the C-bank of detectors recorded at 295, 423, and 573 K are shown in Fig. 2. Rietveld refinement was performed on the profiles recorded at 295 and 573 K. The scattering lengths employed for Li, U, and O were −0.203E-14, 0.84E-14, and 0.581E-14 m, respectively (*10*). The background at ISIS has been found to be well fitted by a fifth-order Chebyshev polynomial (*11*), the coefficients of which are included as refinable parameters. The details of the refinements at 573 and 295 K are given below.

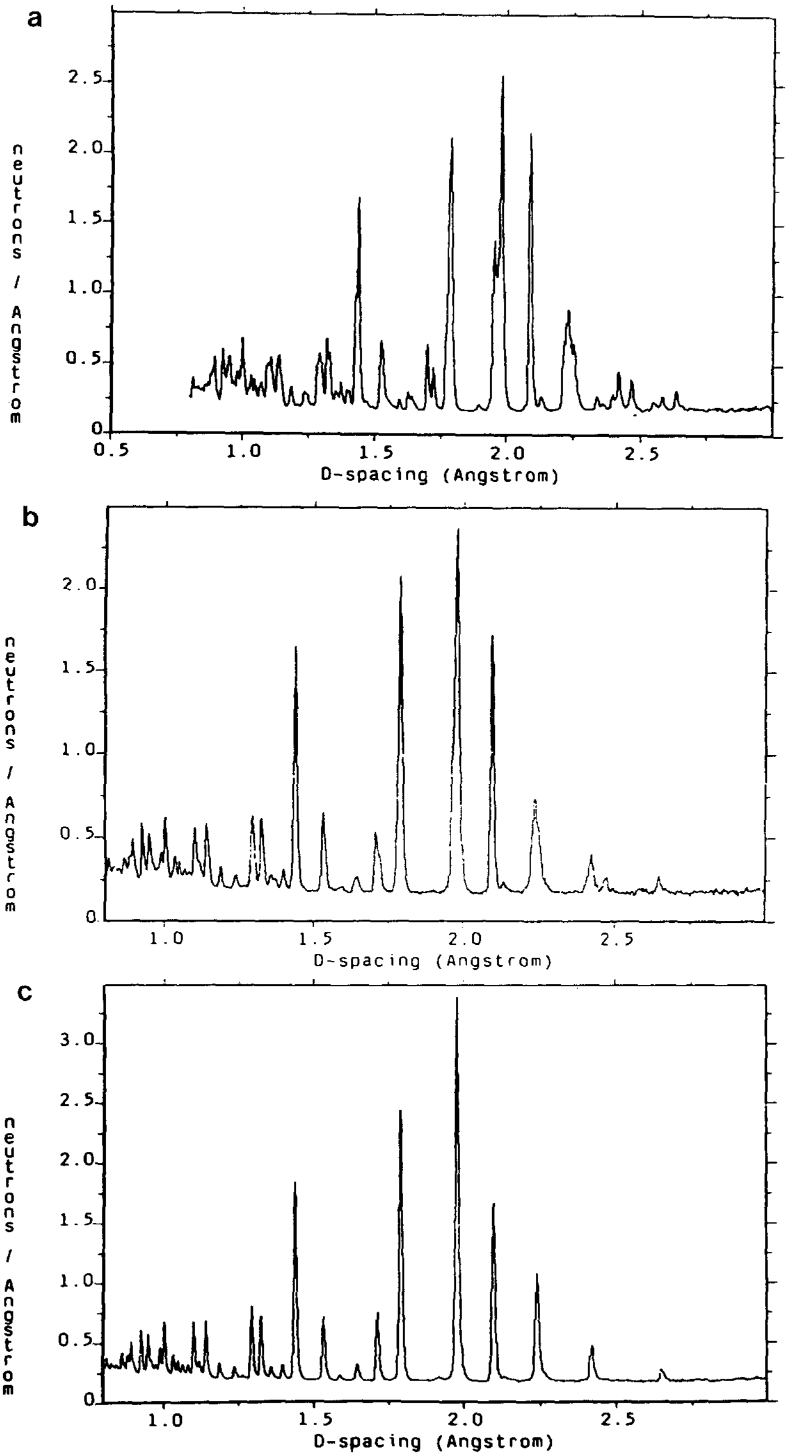

FIG. 2. Neutron profiles for $Li_{0.88}U_3O_8$ recorded on the C-bank of detectors at (a) 295 K, (b) 423 K, and (c) 573 K.

TABLE II

REFINED PARAMETERS $Li_{0.88}U_3O_8$ AT 573 K

Space Group: $P\bar{6}2m$ (No. 189) $Z = 1$
$a = 6.849(3)$ $b = 6.849(3)$ $c = 4.197(1)$ Å

Site	Atom	x	y	z	B(Å^2)	Occ
3f	U_1	0.3542(3)	0.0	0.0	0.68(5)	1.0
3g	O_1	0.3533(7)	0.0	0.5	1.82(9)	1.0
3f	O_2	0.7417(7)	0.0	0.0	2.61(9)	1.0
2c	O_3	0.6667	0.3333	0.0	1.20(9)	1.0
2d	Li_1	0.6667	0.3333	0.5	8.1(3.0)	0.44

Note. $R_p = 3.7\%$, $R_{wp} = 3.9\%$, $R_E = 1.4\%$.

(*a*) *573 K Data*

Refinement of data in the TOF range 4500–19,600 μs was initiated in the space group $P\bar{6}2m$ (No. 189). The coordinates determined by Loopstra (*9*) for the high-temperature form of α-U_3O_8 were taken as starting coordinates for the metal–oxygen framework. Initial refinement of a scale-factor, zero-point, five background and two cell parameters produced an R_{wp} of ~15%. This was reduced further by varying the uranium and oxygen positional parameters along with both Gaussian and Lorentzian peak-shape parameters. Fourier difference maps were then calculated for sections through the xy plane at $0 < z < 0.5$. The only significantly negative features were found for the $z = 0.5$ section which exhibited two such peaks at approximate coordinates of (0.7, 0.3) and (0.3, 0.7). On introducing lithiums at 0.3, 0.7 refinement tended to move them toward the special positions of 1/3, 2/3. They were subsequently placed on this site with an occupancy of 0.44. The final refinement cycles involved 23 variables and resulted in $R_p = 3.7\%$ and $R_{wp} = 3.9\%$. The refinement was insufficiently sensitive to lithium occupancy to allow refinement of the site parameter and this was left at its analytically determined value. The final values of the parameters are given in Table II and the fit of observed and calculated profiles in Fig. 3.

(*b*) *295 K Data*

Atomic coordinates for α-U_3O_8 have been determined at room temperature in the space group *Amm*2 (No. 38) (*12*). These coordinates were utilized as starting coordinates for the uranium–oygen framework. However, in order to facilitate comparison between the orthorhombic and the hexagonal structures, refinement was carried out in an alternative setting, *C*2*mm*, of this space group. The coordinates determined in the above study were transformed by the matrix {00-1/010/100} (*13*).

Data in the TOF range 4500–14,000 μs were utilized in the refinement. Refinement of a scale-factor, zero-point, and five background and three cell parameters proceeded smoothly. Varying the uranium and oxygen coordinates together with Gaussian peak-shape parameters lowered R_{wp} to ~11%. Fourier difference maps were then calculated in sections through xy at $0 < z < 0.5$. The $z = 0.5$ section was the only section to exhibit any peaks of significant density. A number of such peaks were observed, their positions corresponding to sites above each of the in-plane oxygens. There appeared to be no strong preference for one site over another. Lithium was therefore introduced

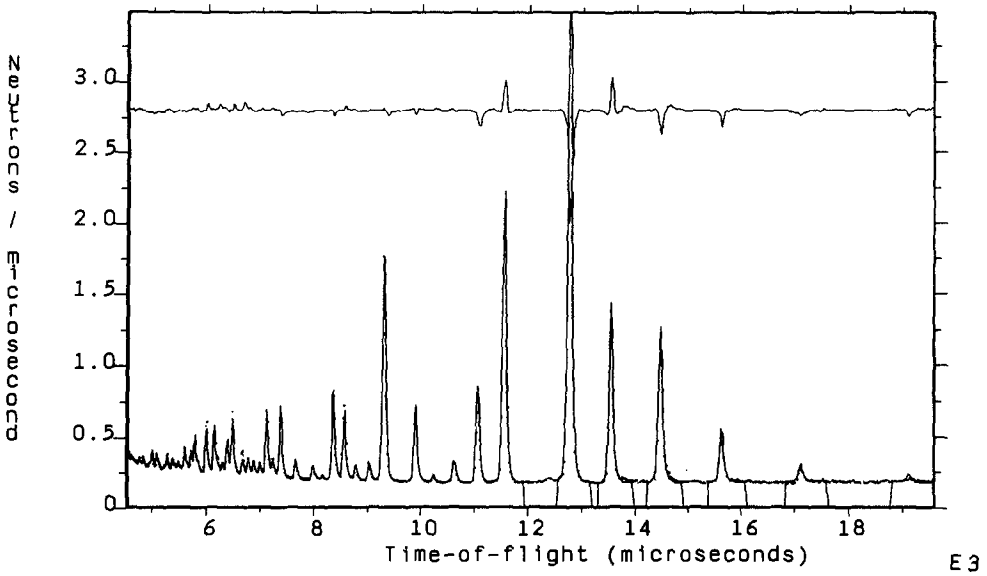

FIG. 3. Observed (points), calculated (full-line), and difference (upper continuous line) profiles for $Li_{0.88}U_3O_8$ at 573 K.

at 2*b* sites (x, 0, 1/2; $x = 0.38$) and two types of 4*e* site (x, y, 1/2; $x = 0.14$, $y = 0.12$; $x = 0.10$, $y = 0.37$). These sites were assumed to be equally and randomly occupied up to the analytically determined composition. The positional parameters were then refined together with the thermal parameters (that for lithium being refined separately and subsequently fixed). Although a reasonable refinement ($R_{wp} = 8.5\%$) was achieved at this stage, the refinement was so insensitive to lithium that the shifts observed for these

TABLE III

REFINED PARAMETERS FOR $Li_{0.88}U_3O_8$ AT 295 K

Space Group: *C2mm* (alternative setting of No. 38) $Z = 2$
$a = 6.9107(8)$ $b = 11.7472(10)$ $c = 4.1919(4)$ Å

Site	Atom	x	y	z	B(Å^2)	Occ
2a	U_1	−0.985(1)	0.0	0.0	0.27(4)	1.0
4d	U_2	0.0	0.3195(4)	0.0	0.27(4)	1.0
2b	O_1	−0.947(2)	0.0	0.5	1.4(1)	1.0
4e	O_2	0.0	0.3216(8)	0.5	1.4(1)	1.0
2a	O_3	−0.555(2)	0.0	0.0	1.4(1)	1.0
4d	O_4	−0.189(2)	0.136(1)	0.0	1.4(1)	1.0
4d	O_5	−0.317(2)	0.340(1)	0.0	1.4(1)	1.0
2b	Li_1	−0.555(2)	0.0	0.5	1.9(−)	0.176
4e	Li_2	−0.189(2)	0.136(1)	0.5	1.9(−)	0.176
4e	Li_3	−0.317(2)	0.340(1)	0.5	1.9(−)	0.176

Note. $R_p = 6.6\%$, $R_{wp} = 8.1\%$, $R_E = 1.4\%$.

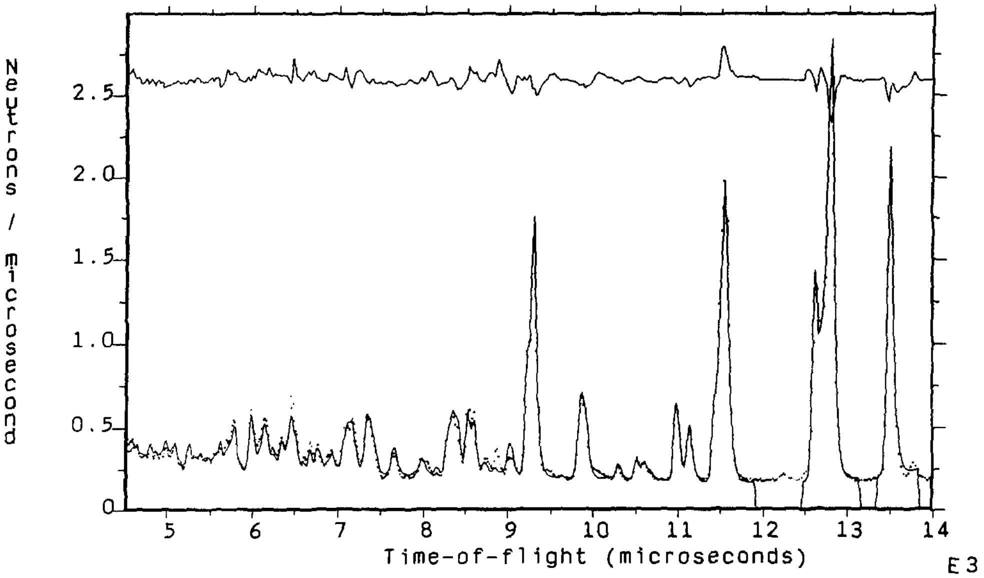

FIG. 4. Observed (points), calculated (full-line), and difference (upper continuous line) profiles for $Li_{0.88}U_3O_8$ at 295 K.

positional parameters were unacceptably large. In addition further refinement cycles resulted in the lithiums moving toward one of the three surrounding in-plane oxygens to the extent that the Li–O bond length became very short (~1.4 Å), considerably less than the sum of the ionic radii quoted by Shannon and Prewitt (~2.1 Å) (*14*). In order to overcome this problem strict constraints were imposed. These constrained the lithiums to lie directly above the corresponding in-plane oxygen. This resulted in only one set

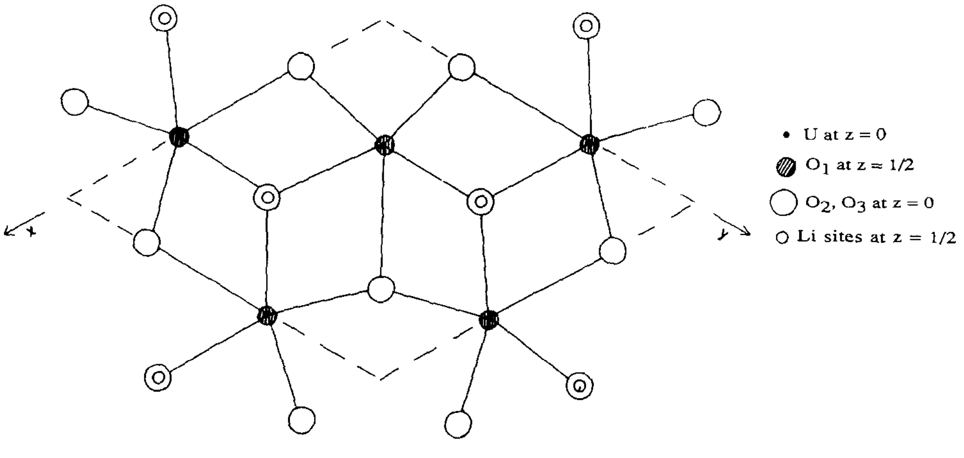

FIG. 5. Projection on (001) of the structure of $Li_{0.88}U_3O_8$ at 573 K.

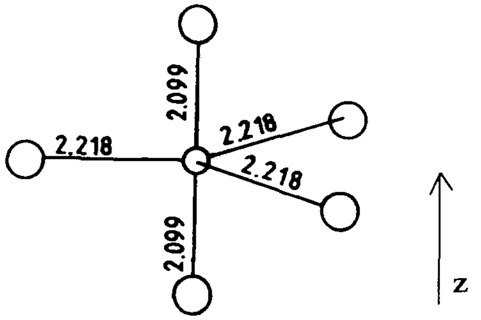

FIG. 6. Trigonal-bipyramidal coordination of lithium (small open circle) by oxygen (large circles).

of positional parameters being refined for each lithium/oxygen combination. The final cycles of refinement involved 20 variables and resulted in $R_p = 6.6\%$ and $R_{wp} = 8.1\%$. The refined parameters are given in Table III and the observed and calculated profiles in Fig. 4.

Discussion

On heating orthorhombic $Li_{0.88}U_3O_8$, the hexagonal product produced has lattice parameters very similar to those of α'-U_3O_8. However, whereas α'-U_3O_8 reverts to α-U_3O_8 on cooling, the insertion compound remains in the hexagonal modification, irrespective of the rate of cooling. It appears that the inserted lithium has stabilized the hexagonal form of the lattice. The endothermic change, accompanied by a slight weight loss, observed in the DTA/TGA at ~80°C may be attributed to the loss of solvent which had not been completely removed by drying under vacuum. The second peak in the DTA trace, the exotherm at ~280°C, is then associated with the structural transformation taking place. This contrasts with the behavior of α-U_3O_8 itself where the $\alpha \rightarrow \alpha'$ transition is believed (from heat capacity data) to be second order and is not accompanied by any features in the DTA.

TABLE IV

SELECTED BOND LENGTHS AND ANGLES IN $Li_{0.88}U_3O_8$ AT 573 K

About U_1	About Li_1
Bond lengths (Å)	
U_1—O_1 2.099(1)	Li_1—O_1 2.218(2)
U_1—O_2 2.654(2), 2.174(2)	Li_1—O_3 2.099
U_1—O_3 2.215(1)	
Angles (°)	
O_1—U_1—O_1 179.7(1)	O_3—Li_1—O_3 180.0
O_1—U_1—O_2 90.2(1), 89.9(1)	O_1—Li_1—O_1 120.0
O_1—U_1—O_3 90.1(1)	
O_2—U_1—O_2 89.7(1)	
O_2—U_1—O_3 63.2(1), 72.0(1)	

Kemmler–Sack and Rüdorff have prepared materials of the form $(Li_2O)_x \cdot UO_2 \cdot UO_3$ (*15*). These were found to have lattice parameters which were close to those of either α- or α'-U_3O_8, depending on the value of x. This, coupled with the tendency of the U_3O_8 framework to persist over a range of oxidation states (*16*), suggests that these materials are very closely related (if not identical with) the ambient-temperature material. At $x = 0.33$ the materials of Kemmler–Sack would correspond to LiU_3O_8. However, from the evidence provided by high-temperature preparations which have been carried out by us (*17*), it seems unlikely that this limiting stoichiometric composition is ever reached, as even at a nominal composition of $Li_{1.0}U_3O_8$ small amounts of a second stable phase are detected. Additionally, at both lower and higher compositions, a mixture of phases, including the hexagonal α'-U_3O_8 type, are found. $Li_{0.88}U_3O_8$ is probably near to the limit of compositional stability for this phase. Some support for this is provided by the open-circuit voltage vs composition curve (*6*), where a fall in voltage (indicative of a single phase region) is observed at $0.25 < x < 0.3$, i.e., before $Li_{1.0}U_3O_8$ is reached.

In the hexagonal form of $Li_{0.88}U_3O_8$, there are only two types of in-plane oxygen, resulting in two types of site for lithium insertion analogous to those found in the orthorhombic form. In contrast with the latter, the lithium ions are not randomly distributed over these sites but appear to show a marked preference for the sites above the O_3 positions. Figure 5 shows a projection of the structure onto the *ab* plane. The lithium is in an almost regular trigonal bipyramidal coordination (Fig. 6), the three in-plane oxygens lying at a slightly longer distance than the ones above and below. The Li–O bond lengths lie in the range 2.0–2.2 Å (Table IV), against a mean value of 2.1 Å for the sum of ionic radii quoted by Shannon and Prewitt, and compare favorably with those observed in other lithium insertion compounds (*18*, *19*). This is an unusual coordination for lithium but one that in this structure apparently optimizes the coordination by oxygen.

The refinement of the room-temperature powder neutron diffraction data is poorer than that of the 573 K data and results in parameters with somewhat larger e.s.d.'s than would perhaps be expected. This is a consequence of two factors. First, the high-temperature material is more crystalline and second, the occupancy of lithium involves a spread over five nearly equivalent sites in the room-temperature form (random distribution) and over only two equivalent sites in the high-temperature form (ordered distribution). This would result in practice in a wider variation in the U–O bond lengths than determined by the diffraction study.

TABLE V

SELECTED BOND LENGTHS AND ANGLES IN $Li_{0.88}U_3O_8$ AT 295 K

	Bond lengths (Å)	
About U_1	About U_2	
U_1—O_1 2.113(2)	U_2—O_2 2.096(1)	
U_1—O_3 2.973(2)	U_2—O_3 2.154(4)	
U_1—O_4 2.130(6)	U_2—O_4 2.524(1), 2.210(3)	
U_1—O_5 2.213(5)	U_2—O_5 2.204(2), 2.257(2)	
About Li_1	About Li_2	About Li_3
Li_1—O_1 2.707(3)	Li_2—O_1 2.315(9)	Li_3—O_1 2.086(9)
Li_1—O_2 2.129(4)	Li_2—O_2 2.544(1), 2.204(2)	Li_3—O_2 2.202(2), 2.278(2)
Li_1—O_3 2.096	Li_2—O_4 2.096	Li_3—O_5 2.096
	Angles (°)	
About U_1	About U_2	
O_1—U_1—O_1 165.8(1)	O_2—U_2—O_2 179.2(1)	
O_1—U_1—O_3 82.9(1)	O_2—U_2—O_3 89.6(1)	
O_1—U_1—O_4 94.8(2)	O_2—U_2—O_4 90.3(1), 89.9(1)	
O_1—U_1—O_5 86.3(2)	O_2—U_2—O_5 90.0(1), 90.3(1)	
O_3—U_1—O_5 58.8(2)	O_3—U_2—O_4 86.7(1)	
O_4—U_1—O_4 95.9(2)	O_3—U_2—O_5 73.2(1)	
O_4—U_1—O_5 73.3(2)	O_4—U_2—O_5 64.8(1), 64.9(1)	
About Li_1	About Li_2	About Li_3
O_3—Li_1—O_3 180.0	O_4—Li_2—O_4 180.0	O_5—Li_3—O_5 180.0
O_1—Li_1—O_2 100.1(3)	O_1—Li_2—O_2 101.4(3)	O_1—Li_3—O_2 121.3(3)
O_2—Li_1—O_2 159.8(3)	O_1—Li_2—O_2 149.8(3)	O_1—Li_3—O_2 122.4(3)
	O_2—Li_2—O_2 108.8(3)	O_2—Li_3—O_2 116.3(3)

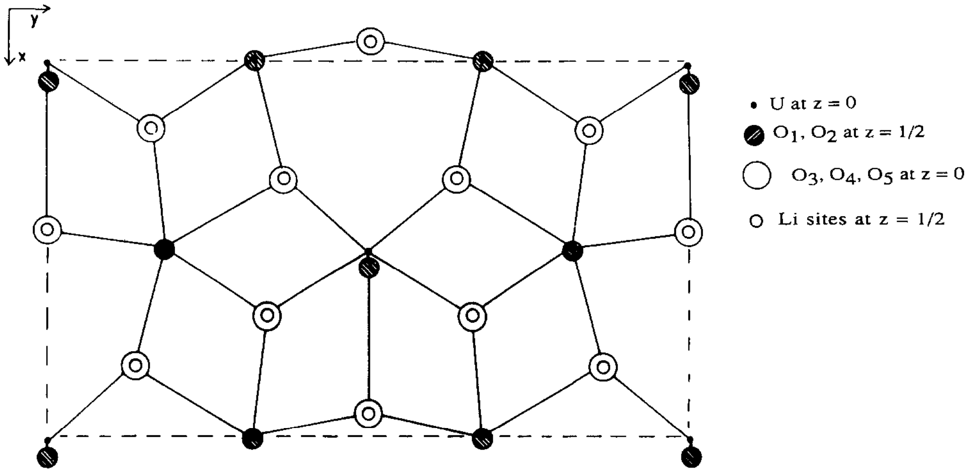

FIG. 7. Projection on (001) of the structure of $Li_{0.88}U_3O_8$ at 295 K.

In addition, the lack of sensitivity of the refinement toward lithium inevitably means that some doubt arises over the precise position of the inserted lithium. Although the Fourier map clearly shows that the inserted lithium resides somewhere above each of the in-plane oxygens, their precise location in the "triangle" formed by the three pillar oxygens is uncertain. This is apparent in the large shifts observed in these parameters, necessitating the constraint that they lie directly above in-plane oxygens (Fig. 7). The Li–O bond lengths, given in Table V, span a larger range (2.1–2.7 Å) than in the hexagonal form, indicating that in the orthorhombic form these sites are too large to allow optimum coordination of lithium by oxygen. Nevertheless, the study does provide support for the view that the insertion process is topotactic as the atomic coordinates of the framework are not substantially different from those of α-U_3O_8 itself. The only significant difference in bond lengths is the increase of ~0.4 Å in the U_I–O_I distance.

It would appear, therefore, that ambient-temperature insertion of lithium into α-U_3O_8, in common with a number of other systems, gives a metastable product. The lithium ions seem to be completely disordered over a number of sites, correlating with the high mobility of the ions at room temperature (*6*). Heating this product causes the metal–oxygen framework to transform to the α'-U_3O_8 structure. This is accompanied by the mobile lithium ions moving to the thermodynamically more favorable sites, resulting in a stable phase.

Acknowledgments

The authors thank Dr. S. Hull of the Rutherford Appleton Laboratory for assistance with the recording of the neutron profiles. A.V.P. thanks the CEGB for a studentship.

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