Thermal expansion in UO_2 determined by high-energy x-ray diffraction

M. Guthrie¹, C. J. Benmore^{2,*}, L.B. Skinner^{2,3}, O.L.G. Alderman^{2,4},
J. K. R. Weber^{2,4}, J. B. Parise^{3,7}, M. Williamson⁵.

- (1) European Spallation Source ESS AB, PO Box 176, SE-221 00, Lund, Sweden
- (2) X-ray Science Division, Argonne National Laboratory, Argonne, IL 60439, USA.
- (3) Mineral Physics Institute, Stony Brook University, Stony Brook, NY 11794-2100, USA.
- (3) Materials Development, Inc., 3090 Daniels Court, Arlington Heights, IL 60004, USA.
- (4) Chemical Science and Engineering, Argonne National Laboratory,
Argonne, IL 60439, USA.
- (5) Nuclear Engineering, Argonne National Laboratory, Argonne, IL 60439, USA.
- (7) Photon Sciences, Brookhaven National Laboratory, Upton, NY 11973, USA

*Corresponding author. E-mail: benmore@aps.anl.gov

Abstract.

Here we present crystallographic analyses of high-energy x-ray diffraction data on polycrystalline UO_2 up to the melting temperature. The Rietveld refinements of our x-ray data are in agreement with previous measurements, but are systematically located around the upper bound of their uncertainty, indicating a slightly steeper trend of thermal expansion compared to established values. This observation is consistent with recent first principles calculations.

1. Introduction

The wide use of UO_2 as fuel in reactor-driven electrical power generation lends significant importance to the characterisation of its thermophysical properties at high temperatures. One critical property is thermal expansion, a design criteria needed to prevent the rupturing of the cladding of fuel rods. In order to minimise the impact of systematic errors from various measurements, Martin [1] collated a series of experimental determinations and fitted these with a simple cubic polynomial. Martin's [1] approach was revisited and updated by Fink in 2000 [2], who recommended retaining Martin's polynomial model. This model has since been encoded as a *de facto* standard used by nuclear engineers worldwide [3]. Microscopic determinations of thermal expansion have several advantages [4]. A correctly calibrated diffractometer gives a direct measurement of the crystal unit cell parameters. In this sense, the measurement gives an absolute measurement of density (and linear dimension) rather than relative to a starting length at a particular temperature. The refined lattice parameters, determined by Bragg peak positions are also unaffected by minor impurities and microstructure that may affect macroscopic measurements.

However, the most recent diffraction studies contributing to the Martin-Fink model are from a 1991 study employing a laboratory based x-ray diffractometer and only reaching 1600 K in temperature [5]. In the 25 years since then, there have been significant technological advances. Correspondingly, we have revisited this issue, conducting a new diffraction study using high-energy x-rays, greatly reducing the otherwise extremely high absorption of the sample. We have also employed a containerless levitation method with laser heating, to reduce the effects of contamination and allow us to collect data up to melting. Such methods have recently led to a substantial revision of the melting curve in the UO_2 - PuO_2 phase diagram [6], and of pure PuO_2 [7], because traditional furnace heating experiments were affected by extensive interaction between the samples and their container. Our new data are in agreement with the thermal expansion given by the Martin-Fink model, but consistently lie in the upper bound of their error-bar, suggesting a slightly steeper trend with temperature.

2. Methods

X-ray experiments have been performed at 11-ID-C and 6-ID-D of the Advanced Photon Source (Argonne, IL, USA). In both cases the scattered x-rays were detected using a Perkin Elmer XRD1621 amorphous silicon area detector. High energy x-rays of 111.16 keV and 100.23 keV (respectively) were used to minimize fluorescence from the K-edge 115.6keV as well as absorption within the sample. The sample-detector distance was calibrated using a NIST standard CeO_2 powder sample. X-ray transmission through the UO_2 sample ~50% was achieved by using a thin incident beam (0.2 mm vertical width) and scanning the sample stage such that diffraction was measured from the top 0.2 mm of the ceramic bead. The samples were supported by aerodynamic levitation, a method that involves floating the sample on a 99.999% purity Ar gas stream inside an Ar

filled chamber [8]. The samples were then heated from above using a 400W CO₂ laser (Synrad Firestar i401). The temperature was measured at the top of the sample using a Chino IR-CAS pyrometer (0.7-0.9 μm waveband). A UO₂ emissivity value of 0.84 $\pm$ 0.03 was used in the temperature correction [2] and the error in temperature is estimated to be $\sim$ 2-3% due to a combination of temperature gradients in the upper part of the sample and chamber window transparency corrections. A brass sheet was placed in front of the area detector to absorb any uranium fluorescence from the L-edges around $\sim$ 20keV, while passing $>$ 80% of the elastically scattered x-rays. Standard corrections were used for polarization, geometric effects, absorption and oblique incidence etc. [9]. The 2D diffraction patterns were integrated using Fit2D [10]. The δQ -resolution of the setup was found to be approximately constant at $\sim$ 0.05 $\text{\AA}^{-1}$ from the FWHM of calibration peaks for $Q < 10 \text{\AA}^{-1}$.

The samples were densely sintered solid spheres of $\sim$ 3mm in diameter and made of UO_{1.999 $\pm$ 0.005} starting material as determined by combustion analysis. Our measurements were performed upon heating only, and there was visible vaporization from the sample surface at the highest temperatures near melting. The maximum oxygen loss at melting is expected to change the stoichiometry to UO_{1.97} based on the thermodynamic relations of Lindemer and Besmann (see equation 43 in [11]). However, in the solid state below the λ -transition the rate of oxygen diffusion is much slower [8, 13]. This level of hypostoichiometry, might be expected to increase the lattice parameter by 0.0016 to 0.0045 $\text{\AA}$ [12]. Since hard x-rays act as a bulk probe, a significant change in the bulk M/O ratio would take several hours to occur on a 3 mm diameter sample. The diffusion coefficient of UO₂ at temperatures of 1700K degrees (assuming $D \sim 5 \times 10^{-8} \text{ cm}^2/\text{s}$ [13]) correlates to a diffusion length of a few tens of microns during a typical 10s heating cycle (comprising of 1-2s diffraction scans). The change in lattice parameter between our pre-heating and recovered samples, measured at room temperature, showed a slight increase in the lattice parameter of +0.0054 $\text{\AA}$, corresponding to a 0.1% change.

3. Crystallographic model

Under ambient conditions, UO₂ crystallises into the fluorite structure with face centred cubic packing within the $Fm\bar{3}m$ space group. The cations locate on the $4a$ Wyckoff sites on the origin while the anions are found on the $8c$ sites at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. Although there is much in the literature concerning a λ -transition in the oxygen sub-lattice (see review in [2]), our data are not strongly sensitive to oxygen locations, so we did not attempt to refine this feature. We conducted Rietveld refinements of our diffraction data using the GSAS [14] and EXPGUI [15] software suites (see **Figure 1** for a typical dataset). In these, a simple isotropic atomic displacement parameter (ADP) was refined for each atom, which gives the only two variables in this crystal structure. The lattice parameter was determined by fitting the position of all observed peaks using the standard Rietveld approach. Additional variables in the refinements described the Bragg peak widths and the experimental background. Additionally, the possibility of preferred

orientation was explored, however, this parameter consistently refined to a value of ~ 1.0 indicating complete orientational averaging.

Figure 1. Typical powder diffraction pattern obtained from a sample at a temperature of 300K. The measured diffraction intensities are shown as open circles, while the fit is the solid line running through these. Below the fitted pattern the residual shows the difference between observed and calculated intensity. The inset shows the high $Q = 4\pi \sin(\vartheta) / \lambda$ (where $\lambda = 0.112 \text{ \AA}$ is the x-ray wavelength and 2ϑ is the scattering angle) part of the fit at a magnified scale.

4. Results and Discussion

Our room temperature data provide a benchmark to compare with previous studies. Our ambient temperature lattice parameter of $5.477 \text{ \AA}$ was significantly longer than the literature value of $5.4699 \text{ \AA}$ [12]. This difference was attributed to an effect of sample mass absorption by the x-rays, which effectively shifts the centre of mass of diffraction upstream. Correspondingly, ambient pressure lattice parameter was fixed at the literature value of $5.468 \text{ \AA}$ and the transparency correction included in GSAS was refined to take account of the offset. This correction has a single parameter T_s , which was determined by refining the ambient temperature dataset. Thereafter, at higher temperatures, T_s was fixed and the lattice parameters were refined and compared to the Martin-Fink model.

Previously, Martin [1] examined data from 15 different measurements and expressed them all as relative linear thermal expansion $\Delta L/L$ relative to a nominal value at 273 K. Thus, $\Delta L/L = (L_T - L_{273})/L_{273}$ where L_T is the absolute length at temperature T and expressed in percent. After excluding outlying datasets, Martin fitted the complete dataset using a cubic polynomial with the four coefficients k_i .

$$L = L_{273}(k_0 + k_1T + k_2T^2 + k_3T^3)$$

In order to obtain a better fit, Martin also divided the data into two temperature ranges: $273 \leq T \leq 923$ and $923 \leq T \leq 3120$ and the corresponding parameters are quoted in Table 1.

Table 1 Fitted coefficients of Martin's polynomial model [1].

Coefficient	Temperature range (K)	
	273 - 923	923 – 3120
k_0	0.99734	0.99672
$k_1 (\text{K}^{-1})$	0.9802×10^{-6}	1.179×10^{-5}
$k_2 (\text{K}^{-2})$	-2.705×10^{-10}	-2.429×10^{-9}
$k_3 (\text{K}^{-3})$	24.291×10^{-13}	1.219×10^{-12}

In the review by Fink [2] more recent data and some of the outliers originally excluded by Martin [1] were added. However, the resulting fit gave values that differed little from those of Martin. Fink recommended that these were retained, although that the uncertainties were increased.

Our diffraction data are shown plotted with the Martin polynomial and Fink's uncertainties in **Figure 2**. Notably our data are systematically offset to higher values of relative linear expansion than the Martin-Fink values, by $\sim 0.3\%$, and lie on the upper uncertainty bound given by Fink [2]. We note that our findings are in agreement with a recent first-principles study by Yun et al. [16] who also found an elevated thermal expansion coefficients. We also considered the effect of possible reduction in oxygen content on the refined lattice parameters. As discussed above, this could lead to a maximum increase of $0.0045 \text{ \AA}$ [12]. After taking this into account, our values for relative linear expansion are still $\sim 0.2\%$ in excess of Martin-Fink.

Figure 2. The reference relative thermal expansion of Martin [1] (solid line), with the uncertainty limits of Fink (dashed lines) [2] are shown in blue. Our own data are shown in red along with our estimated standard deviations.

An independent check of our pyrometry temperature measurement comes from the microscopic atomic displacement parameter (ADP's) of the U atoms. Physically, this measures the extent of the deviation of the instantaneous atomic position from the average crystallographic site. This manifests in the diffraction data as a drop-off of measured intensities with angle. Figure 3 shows the refined values of our uranium ADPs $U_{iso}(U)$ as a function of temperature and compares with Hutchings *et al.* [17]. Within the experimental uncertainty, good agreement with $U_{iso}(U)$ is found across the entire range of the measurement. Taken together with our measured T_m , our temperature measurements appear to be robust.

Figure 3. Isotropic thermal parameter for Uranium atoms (left) in UO_2 as a function of temperature compared with Hutchings *et al* [17].

5. Conclusions.

The high-energy x-ray diffraction data we present here provide new microscopic measurement of the thermal expansion of UO_2 . Our data show a thermal expansion that is systematically slightly higher than standard reference data [1, 2], which are based on measurements that are now 25 years old. The use of containerless methods, which eliminate the sample-containment vessel interaction, combined with laser beam heating provide a new and accurate capability for the characterization of nuclear materials at extreme conditions.

6. Acknowledgements

We thank Rick Spence and Dr. Doug Robinson for technical support during the experiments and for useful discussions. Dr. Marius Stan is thanked for useful discussions. The Advanced Photon Source, Argonne National Laboratory, is funded under U.S. DOE, BES, contract number DE-AC02-06CH11357. This work was also supported by the U.S. Department of Energy (DOE), Small Business Innovation Research grant DE SC0007564 (x-ray experiment, J.K.R.W., O.L.G.A.) and the Office of Basic Energy Sciences (BES) grant DE-FG02-09ER46650 (L.B.S. and J.B.P).

References.

- [1] D.G. Martin, Journal of Nuclear Materials 152 (1988) 94-101.
- [2] J. K. Fink, Journal of Nuclear Materials 279 (2000) 1–18.
- [3] Thermophysical properties of materials for nuclear engineering, IAEA, Vienna (2008) www-pub.iaea.org/MTCD/publications/PDF/IAEA-THPH_web.pdf
- [4] R.S. Krishnan, R. Srinivasan, R. Devanarayanan, Thermal expansion of crystals. Pergamon Press, Oxford, 1970.
- [5] A.C. Momin, E.B. Mirza, M.D. Mathews, Journal of Nuclear Materials 185 (1991) 308-310.
- [6] R. Bohler et al., Journal of Nuclear Materials 448 (2014) 330.
- [7] F. De Bruyker et al., Materials Today 13 (2010) 52.
- [8] L. B. Skinner et al., Science 346 (2014) 984-987.
- [9] L.B. Skinner, C.J. Benmore, J.B. Parise, Nuc. Instr. & Methods A 662 (2012) 61-70.
- [10] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, D. Hausermann, High Pressure Res 14 (1996) 235.
- [11] T.B. Lindemer and T.M. Besmann, J. Nuc. Mat. 130 (1985) 473.
- [12] G. Leinders, T. Cardinaels, K. Binnemans, M Verwerft, Journal of Nuclear Materials 459 (2015) 135-142.
- [13] G.E. Murch, C.R.A. Catlow, J. Chem. Soc., Faraday Trans. 2,83 (1987) 1157.
- [14] A.C. Larson and R.B. Von Dreele, General Structure Analysis System (GSAS), Los. Alamos National Laboratory Report LAUR 86-748 (2004).
- [15] B.H. Toby, Journal of Applied Crystallography 34 (2001) 210-213.
- [16] Yun et al., Journal of Nuclear Materials 426 (1-3) (2012) 109-114.
- [17] M.T. Hutchings, J. Chem. Soc. Farad. Trans. 2, 83 (1987) 1083-1103.