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Coherent neutron scattering length of ^{18}O.

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Analysis of neutron data from an ^{18}O-enriched single crystal of $UO_{2\cdot010}$ has realized a value of 6·01 (0·13) fermi units for the thermal neutron scattering length of ^{18}O.

The coherent neutron scattering length of ^{18}O has been determined as part of a programme of work on the crystal structures of the actinide oxides using neutron diffraction methods to improve the definition of oxygen atoms over that realized in the earlier X-ray analyses. It has proved difficult to establish the positions and occupation numbers of interstitial atoms, particularly when these occupation numbers are low as, for example, in the case of $UO_{2\cdot13}$ (Willis, 1963). One possible approach to the problem is to use the neutron spectra from two crystals each containing a different isotope of oxygen. If the scattering lengths of the isotopes are substantially different the oxygen atoms could be located by difference-Patterson analysis and refined by least squares. The scattering length of ^{18}O has therefore been estimated in order to determine if ^{16}O and ^{18}O are suitable isotopes for this isotope-replacement technique.

Single crystals of ^{18}O-enriched natural UO_2 were used in the experiment. The structure of UO_2 conforms to the fluorite cubic space group *Fm*3*m*, with metal atoms at the four Wyckoff (*a*) positions and oxygen atoms at the eight (*c*) positions. Therefore, for a model in which the atoms execute harmonic vibrations, the refinable parameters are the scattering lengths and isotropic thermal coefficients for uranium and oxygen, and the scale factor. Willis & Rouse (1966) have refined the structure of natural UO_2 with non-absolute neutron intensities by fixing the scattering length of natural oxygen at 5·77f* (Hughes & Schwartz, 1958). The value they obtained for the natural uranium scattering length, 8·32(4)f, was treated as an invariant in the present investigation.

Spherical crystals of UO_2 were enriched with ^{18}O by equilibrating them at 1425°C with a CO_2/CO mixture containing approximately 90% of ^{18}O. Subsequent mass spectrometric analysis of the CO_2/CO gas mixture gave the following estimate for the oxygen isotopic ratio:

$$^{18}O:{}^{16}O = 4{\cdot}89(6):1{\cdot}00\,.$$

The stoichiometric composition of the samples, estimated by measuring the oxygen potential with a high-temperature galvanic cell (Markin & Bones, 1962), was $UO_{2\cdot010\pm0\cdot004}$.

Neutron diffraction intensities were recorded at the A.E.R.E. PLUTO reactor with an automated Ferranti four-circle diffractometer. The neutron beam directed at the specimen was obtained by reflexion from the (422) planes of a copper single crystal and had a mean wavelength of 1·046 Å. The integrated intensities were measured by the 2θ-scan technique, counts being recorded against a monitored incident beam. Initially a set of intensities was measured for a number of reflexions belonging to each of the three reflexion clases, $h+k+l=4n$ (strong), $4n\pm1$ (medium) and $4n+2$ (weak). Refinement of the structure on these preliminary data showed that the $4n$ class of reflexions displayed marked extinction effects. On this basis a number of $4n\pm1$ and $4n+2$ reflexions were selected and, for each of these, the intensities I_i ($i=1,2,\ldots,n$) of all n equivalent but physically distinct reflexions were measured. The n intensity values were averaged and the variance, $\sigma^2(I)$, of the mean intensity, I, was estimated on the basis of population statistics using the expression

$$\sigma^2(I)=\{\sum_{i=1}^{n}(I_i-I)^2\}/n(n-1)\,.$$

Absorption corrections were not necessary since the small value of μR for the spherical specimen, 0·025, defines a constant transmission factor for each reflexion.

The refinement was conducted by full-matrix least squares with the program of Busing, Martin & Levy (1962). The scale factor, isotropic thermal parameters, and the effective oxygen scattering length were refined in the usual manner by minimizing the function $\Sigma\,w(F_o-kF_c)^2$; weighting factors w were assigned according to

$$w=\left\{\frac{\sigma(I)}{I}\cdot\frac{F_o}{2}\right\}^{-2}$$

which corresponds to the inverse variance of $|F_o|$. The final set of observed and calculated structure factors is listed in Table 1. The discrepancy index R of 0·0073 compares favourably with the value of 0·0059 for the 'expected R index' which is given by $0{\cdot}7979\ \Sigma\,\sigma(|F_o|)/\Sigma\,|F_o|$. Further evidence for the reliability of the final model is found by comparing the thermal parameters with those obtained by Willis & Rouse for natural UO_2 (Table 2). A more quantitive criterion of the model's reliability is the application of the χ^2 test to the F_o and F_c sets. For the eleven independent reflexions, the function

$$T^2=\Sigma\,\{(F_o-F_c)/\sigma(F_o)\}^2$$

is distributed as χ^2 (*International Tables for X-ray Crystallography*, 1959) with eleven degrees of freedom. T^2 has a value of 16·99, which gives a probability of 0·112 that the calculated structure factor set varies randomly from the parent (F_o) distribution, *i.e.* the F_o and F_c sets are in agreement at the 11·2% significance level. It can be concluded therefore that at this level, the parameter standard deviation estimates are reliable. Moreover, it can be stated safely that the assumption made in the refinement, *viz.* that the stoichiometric composition of the specimen was $UO_{2\cdot000}$ rather than the observed $UO_{2\cdot010}$, was reasonable at this level.

The least-squares value determined for the effective oxygen scattering length was 5·97(5)f which corresponds to a scattering length of 6·01(13)f for ^{18}O since ^{16}O can be safely assigned the scattering length of natural oxygen. The isotope-replacement method is therefore unsuitable for ^{16}O and ^{18}O as their scattering lengths are so similar. This is

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* The symbol f designates the fermi unit, 10^{-13} cm

Table 1. *Observed and calculated structure factors*

	h	k	l	$\lvert F_o\rvert$	kF_c*	$\lvert F_o\rvert - \lvert F_c\rvert$	$\sigma(\lvert F_o\rvert)$
$(4n\pm1)$							
	5	1	1	60·00	60·29	−0·29	0·23
	5	3	1	59·57	59·47	0·10	0·16
	5	5	1	58·13	57·84	0·29	0·15
	7	1	1	57·73	57·84	−0·11	0·22
	5	5	3	57·26	57·05	0·21	0·42
	7	3	1	56·65	57·05	−0·40	0·20
$(4n+2)$							
	4	2	0	23·21	−23·12	0·09	0·23
	4	4	2	20·19	−19·89	0·30	0·32
	6	0	0	19·30	−19·89	−0·59	0·28
	6	2	2	18·95	−18·36	0·59	0·60
	6	4	0	17·17	−16·90	0·27	0·49

* $k=0·316$ (3)

Table 2. *Isotropic thermal parameters*

	B_U	B_O
Present analysis	0·207 (23) Å^2	0·448 (37) Å^2
Willis & Rouse (1966)	0·214 (8)	0·432 (12)

a disappointing result, but it will at least terminate speculation about the use of ^{18}O for this purpose.

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Neutron diffraction study of hydroxylammonium chloride, NH$_3$OHCl.

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The structure of hydroxylammonium chloride, NH$_3$OHCl, has been studied with the use of partial three-dimensional neutron diffraction data, to a final $R=8$%. The heavy atom coordinates reported by Jerslev (1948) by X-ray studies are more or less confirmed. The hydrogen atoms have been located and their positions refined. The N-O distance is 1·383 Å, much shorter than the value 1·47 Å reported by Jerslev. The NH$_3$ group is in the form of an undistorted triangular pyramid in the crystal. The average of the N-H distances is 1·044 Å. The O-H bond length is 0·996 Å and all the hydrogens are bonded to chlorines of the neighbouring molecules.

The crystal structure of NH$_3$OHCl has been studied earlier by X-ray methods (Jerslev, 1948). The present neutron diffraction investigation was undertaken primarily for the purpose of locating the hydrogen atoms and it has also resulted in an improvement of all the position parameters.

Crystals of hydroxylammonium chloride were grown by the method described by Jerslev (1948). The crystal used for collecting the data was in the form of a cylinder (1·8 × 5·2 mm) and mounted on a two-circle goniometer set so that the b axis of the crystal was along the φ axis of the goniometer and the scattering vector remained in the χ plane for all reflexions. The space group and unit cell as determined by X-rays and neutrons are $P2_1/c$, $Z=4$, $a=6·95$, $b=5·95$, $c=7·70$ Å, $\beta=120·8°$ in agreement with previous X-ray results. Intensities of 320 $h0l$, $0kl$ and some hkl reflexions were measured on the instrument at the Oak Ridge research reactor, using the θ-2θ scan technique ($\lambda=1·077$ Å). The data were corrected for absorption by the method of Busing & Levy (1957). The intensities were reduced to structure factors in the usual way by comparison with the 400 reflexion from a standard sodium chloride crystal. No correction for extinction was made because of the good agreement between intensity measurements from two different sized crystals. Nuclear density projections were first drawn on (010) and (100) planes, based on neutron amplitudes and phases derived from the parameters of heavy