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Neutron Diffraction Study of β-Uranium Pentafluoride between 77 and 403 K

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The structure of β-UF_5 has been refined by neutron powder profile analyses at 77, 293, 348, and 403 K. The structure is relatively temperature insensitive within this range and at 403 K there is a slow conversion to α-UF_5. The coordination polyhedron may be described as either a square antiprism or a dodecahedron, the former polyhedron giving the better fit with the observed atomic positions.

1. Introduction

In an X-ray powder study, Zachariasen (*1*) found β-UF_5 to be tetragonal, space group $I\bar{4}2d$, with $a = 11.473$, $c = 5.208$ Å, and proposed fluorine coordinates based on spatial considerations. In a later X-ray study, Ryan *et al.* (*2*) corrected one of the fluorine positions. In β-UF_5, the uranium atom is 8-coordinate with a polyhedron intermediate between a square antiprism and a dodecahedron.

β-UF_5 transforms slowly to α-UF_5 at about 403 K (*3*), and the α-UF_5 structure has been reported to be 6-coordinate (*4*). It was thought worthwhile to investigate the β-UF_5 structure with the neutron powder profile technique, between 77 K and the transition temperature, to study temperature dependence of the structure, especially near the transition where a major reconstruction apparently occurs.

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2. Experimental and Structure Refinements

About 20 g of β-UF_5 was prepared by condensing excess UF_6 onto a slurry of approximately 10 g of UF_4 in HF. The mixture was stirred in a Kel-F tube for several days at room temperature. The volatile materials (excess UF_6 and HF) were then removed under vacuum. The UF_5 was transferred to another Kel-F tube in a dry box, and the latter was then removed and placed in a cryostat (*5*). The temperatures above 293 K were obtained by using oil and an immersion heater instead of liquid nitrogen in the cryostat. Neutron powder patterns were collected at the 6HB diffractometer on the AAEC materials testing reactor HIFAR, with the elastic diffraction technique (*6*), to $2\theta = 70°$ with $\lambda = 1.080$ Å.

Initial runs showed an unidentified impurity with peaks at $2\theta = 27.5$, 31, and 42°. Prolonged pumping of the sample reduced the impurity level, but it could not be completely removed.

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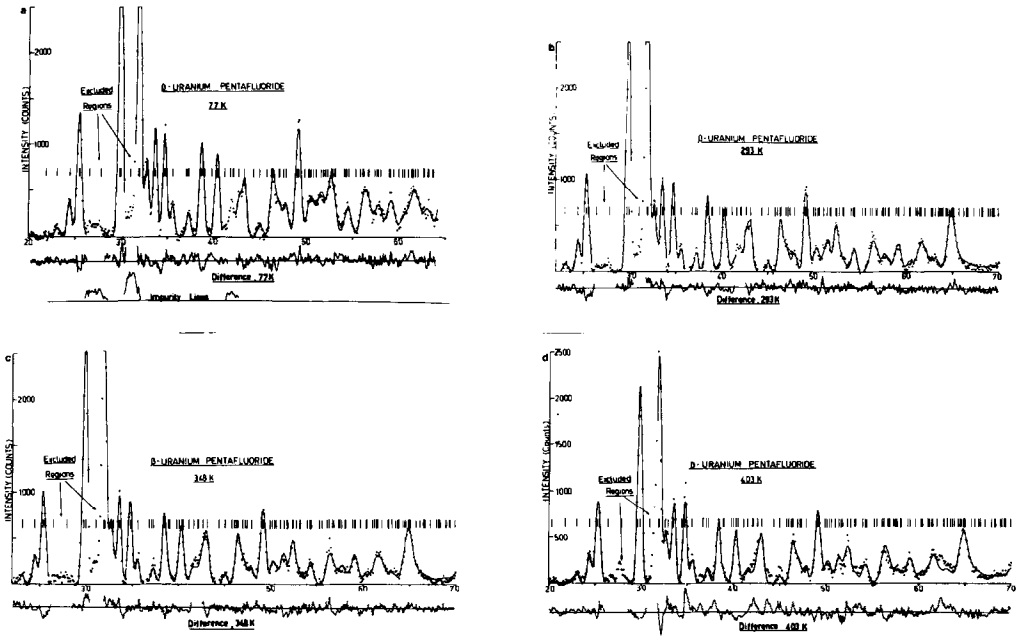

FIG. 1 (a–d). Observed and calculated neutron powder profiles and their differences for β-UF_5 at 77, 293, 348, and 403 K. The step interval is 0.1° 2θ, and the background levels are 500–800 counts.

Profile refinements were made with the Rietveld computer program as modified by Hewat (*7*) with $b(U) = 8.5$ fm and $b(F) = 5.6$ fm. As the Kel-F peak obscured the low-angle region, the data above $2\theta = 20°$ were used. Preferred orientation and asymmetry corrections were not necessary. The observed and calculated profiles are given in Figs. 1a to d. The difference plots show that excluding the three regions reduced to an acceptable level the influence of the impurity. Below Fig. 1a is given the average of the residual impurity peaks for the 77, 293, and 348 K data. Their intensity suggests an impurity level of about 5%. The positional parameters at the various temperatures are given in Table I and other profile parameters in Table II.

3. Discussion

The profile refinements between 77 and 403 K are all consistent with the β-UF_5 structure of Ryan *et al.* (*2*). The β-UF_5 structure is shown to be insensitive to temperature over this range; the changes in the unit cell dimensions and the positional parameters in Tables I and II are quite small. The difference plot for the 403 K refinement shows additional lines beginning to appear which are due to the slow formation of α-UF_5 (these also cause an increase in the R factor for the 403 K refinement). As the 403 K pattern was collected over 2 days, it is evident that complete transformation to α-UF_5 would take a long time. The transformation temperature is not sharply defined and the transformation is sluggish and reconstructive (*9*).

Ryan *et al.* (*2*) suggest the 8-coordinate polyhedron in β-UF_5 is intermediate between a square antiprism and a dodecahedron. Ideal square antiprisms and dodecahedra were fitted to the neutron coordinates with a computer program (*10*). The equiangular square antiprism fitted in 16 orienta-

TABLE I

POSITIONAL PARAMETERS FROM THE 77, 293, 348, AND 403 K NEUTRON DATA

Temp (K)	10^4x(U)	10^4x(U)	10^4y(F(1))	10^4z(F(1))	10^4x(F(2))	10^4x(F(3))	10^4y(F(3))	10^4z(F(3))	Overall B (Å^2)
403	871(11)	449(11)	1681(11)	4453(19)	−2700(12)	1450(9)	760(10)	77(20)	1.4(1)
348	847(8)	426(8)	1708(8)	4396(14)	−2741(8)	1450(7)	763(7)	92(14)	1.9(1)
293	853(7)	421(7)	1706(7)	4357(13)	−2750(7)	1442(6)	749(6)	96(13)	2.1(1)
77	860(8)	405(7)	1692(8)	4449(14)	−2776(8)	1457(6)	766(7)	52(14)	0.8(1)
X Ray(2)	876(1)	391(20)	1686(21)	4389(44)	−2736(27)	1456(18)	757(20)	36(39)	

TABLE II

EXPERIMENTAL DETAILS, R FACTORS, AND UNIT CELL AND HALF-WIDTH PARAMETERS FOR THE 77, 293, 348, AND 403 K NEUTRON PROFILE REFINEMENTS OF THE β-UF_5 STRUCTURE

Temp (K)	2θ Range (°)	Excluded regions (°2θ)	No. of reflections in pattern	R^a	R(expected)^a	Residual^a	a (Å)	c (Å)	10^3U^a	10^3V^a	10^3W^a	10^2z^a
403	20–70	26.2–28.5, 30.7–31.6	146	16.4	9.5	3.7	11.469(5)	5.215(2)	71(11)	−40(8)	8(1)	9(2)
348	22–70	26.3–28.4, 30.5–31.6 41.5–42.5	146	11.6	8.6	2.0	11.471(3)	5.212(3)	66(7)	−39(6)	8(1)	15(1)
293	22–70	26.3–28.3, 30.5–31.6 41.6–42.3	146	10.9	8.5	1.8	11.473(3)	5.208(2)	51(6)	−31(5)	7(1)	16(1)
77	20–65	26.3–28.0, 30.5–31.5 41.6–42.3	116	10.0	7.3	2.4	11.477(3)	5.175(2)	73(8)	−43(6)	9(1)	16(1)

^{a} $R = 100\times \Sigma(|y_0 - (1/c)y_c|)/\Sigma y_0$; R(expected) $= 100\times ((N - P)/\Sigma w y_0^2)^{1/2}$; Residual $= \Sigma w(y_0 - (1/c)y_c)^2/(N - P)$. U, V, W are half-width (h) parameters, where $h^2 = U\tan^2\theta + V\tan\theta + W$; Z is the instrument zero in degrees 2θ. Other terms are defined in Ref. (7).

tions with an rms interbond angle error of 0.37°, while the normalized dodecahedron fitted in 8 ways with an rms error of 0.54°. This confirms the earlier conclusion that the polyhedron in β-UF_5 may be described in either way.

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