JOURNAL OF SOLID STATE CHEMISTRY 45, 396–398 (1982)

Crystallographic Parameters in α-UF_5 and U_2F_9 by Multiphase Refinement of High-Resolution Neutron Powder Data

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Received June 1, 1982

The crystal structures of α-UF_5 and U_2F_9 were refined with high-resolution neutron powder diffraction data from an α-UF_5/U_2F_9 mixture. Refinement was achieved by a multiphase Rietveld profile refinement technique. The results are compared with previous X-ray and neutron powder studies.

Introduction

Zachariasen (*1, 2*) deduced atomic positions in α-UF_5 and U_2F_9 from X-ray powder diffraction data and a consideration of packing possibilities. Laveissière (*3*) confirmed the U_2F_9 structure in a powder neutron study. Eller *et al.* (*4*) refined both structures with X-ray single-crystal data. They found a 0.2-Å correction to the x(F(2)) parameter in α-UF_5 but their value of 0.2216(5) for x(F(1)) in U_2F_9 differed significantly from the Laveissière value of 0.2276(10). As our laboratory now has a high-resolution neutron powder diffractometer (HRD), with half-widths of ~0.25° in the range $0 < 2\theta < 160°$, it seemed worthwhile to reexamine these structures with this instrument in order to check the 0.2-Å shift in α-UF_5 and the x(F(1)) parameter in U_2F_9. Data were obtained from α-UF_5 and U_2F_9 in a mixture, which was not difficult to pre-

TABLE I

MULTIPHASE PROFILE REFINEMENT OF HRD NEUTRON DATA FROM α-UF_5/U_2F_9 MIXTURE

R (weighted profile)	$= (\Sigma w(y_0 - y_c)^2/\Sigma w y_0^2)^{1/2}$	$= 0.157$
R (expected)	$= ((NO - NV)/\Sigma w y_0^2)^{1/2}$	$= 0.100$
Bragg R	$= \Sigma\lvert I_0 - I_c\rvert/\Sigma I_0$	$= 0.052$ (α-UF_5)
		$= 0.030$ (U_2F_9)
Goodness of fit	$= \Sigma w(y_0 - y_c)^2/(NO - NV)$	$= 2.44$
Preferred orientation for α-UF_5 (110 vector) G		$= 0.099(10)$
Asymmetry parameter	$= 0.17(1)$	
Half-width parameters	$U = 0.086(7)$, $V = -0.105(17)$, $W = 0.151(8)$	
	where $H^2 = U \tan^2\theta + V \tan\theta + W$	

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0022-4596/82/150396-03$02.00/0

pare. To analyze this data, the multiphase profile refinement method was employed.

Experimental and Refinement

An α-UF_5/U_2F_9 mixture was prepared by heating a β-UF_5 sample from a previous study (*5*) at 180°C until there was no further change (in 24 hr) in the diffraction pattern. Neutron powder data to 2θ = 160° were collected on the HRD, the sample being held in a quartz tube. The value of λ was fixed at 1.8928 Å, which gave a = 8.4716 Å for U_2F_9. Refinement was achieved with the two-phase program of Wiles and Young (*6*), with corrections and an improved asymmetry function (*7*). The scattering lengths were taken as b(U) = 8.61 fm and b(F) = 5.66 fm. A preferred orientation correction was necessary for α-UF_5 but not for U_2F_9. Gaussian peaks were assumed. The presence of impurity was largely accounted for by excluding six 2θ regions of width 0.5 to 1.5° 2θ. The impurity could not be identified from published patterns, but it may have been UOF_2 (*4*).

The results of the multiphase refinement are given in Table I and Fig. 1.

Discussion

(*a*) α-*UF_5*. Our value for the x(F(2)) parameter in α-UF_5, 0.2885(9) (Table II), is in agreement with the X-ray value of 0.285(1) of Eller *et al.* (*4*); thus the shift of 0.2 Å from the Zachariasen value (0.315) is confirmed. Our y(F(2)) parameter is also in agreement with the X-ray value of Eller *et al.* (*4*), confirming the validity of their discussion of the α-UF_5 structure in terms of bond length–bond strength correlations.

(*b*) *U_2F_9*. The present HRD value of 0.2262(13) for x(F(1)) (Table III) agrees well with the Laveissière (*3*) value, whereas the Eller *et al.* (*4*) value is about 3σ lower. As the neutron data are more sensitive to the fluorine contribution, suggested parameters

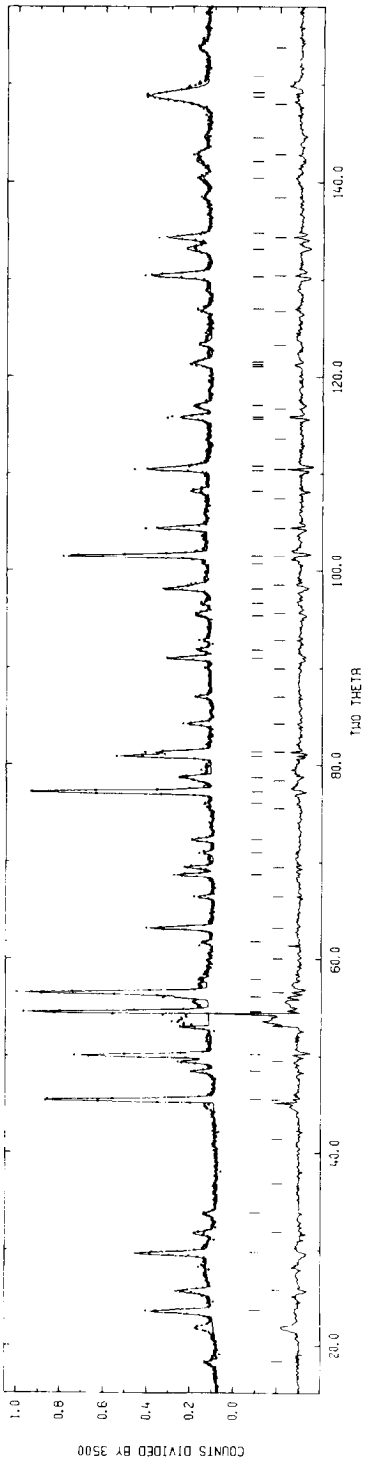

FIG. 1. Profile refinement for the α-UF_5/U_2F_9 mixtures. The observed data are indicated by crosses, and the calculated results by a solid line. Markers directly beneath the pattern indicate the positions of α-UF_5 reflections, and those below these are the positions of U_2F_9 reflections. A difference curve appears at the bottom—peaks in this curve are attributed to an impurity, possibly UOF_2.

TABLE II

PARAMETERS FOR α-UF_5

Study	x(F(2))	y(F(2))	a (Å)	c (Å)	B_U	B_F
Zachariasen X-ray	0.315	0.113	6.525	4.472	—	—
Eller *et al.* X-ray	0.285(1)	0.113(1)	6.518(4)	4.470(1)	—	—
Present study neutron	0.2885(9)	0.1123(8)	6.5259(3)	4.4717(2)	1.68(11)	2.39(8)

TABLE III

PARAMETERS FOR U_2F_9

Study	x(U)	x(F(1))	x(F(2))	z(F(2))	B_U	B_F
Zachariasen X-ray	0.187	0.225	0.20	0.46	—	—
Laveissière neutron	0.1888(4)	0.2276(10)	0.2059(9)	0.4419(7)	—	—
Eller *et al.* X-ray	0.1877(2)	0.2216(5)	0.2087(18)	0.447(29)	—	—
Present study neutron	0.1884(6)	0.2262(13)	0.2078(5)	0.4425(8)	0.28(14)	1.30(13)

for U_2F_9 are the average of the present and Laveissière (*3*) studies.

This study illustrates the effectiveness of the multiphase profile refinement method when used in conjunction with high-resolution neutron powder data.

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