

Supplementary Information

Tilting and Distortion in Rutile Related Mixed Metal Ternary Uranium Oxides: A Structural, Spectroscopic and Theoretical Investigation

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Section S1: Refined Structural Parameters for MnUO₄, CoUO₄ and MgUO₄.

Table S1. Structural parameters for MnUO₄ obtained from joint refinements in space group *Ibmm* against NPD and SXRD data recorded at $\lambda = 1.622$ and 0.77637 Å respectively. $a = 6.75418(2)$ Å, $b = 6.64819(2)$ Å, $c = 6.98642(2)$ Å. $R_p = 2.82\%$, $wR_p = 3.87\%$, $\chi^2 = 8.654$.

Atom	Site	x	y	z	U_{iso} (x100 Å ²)
Mn	4 <i>b</i>	0.5	0	0	0.368(17)
U	4 <i>e</i>	0.01521(5)	0	0.25	1.3132(32)
O1	8 <i>i</i>	0.01101(66)	0.28814(34)	0.25	0.96(6)
O2	8 <i>h</i>	0.18779(35)	0	-0.0107(8)	1.14(6)

Table S2. Structural parameters for CoUO₄ obtained from joint refinements in space group *Ibmm* against NPD and SXRD data recorded at $\lambda = 2.439$ and 0.77637 Å respectively. $a = 6.49717(1)$ Å, $b = 6.50584(1)$ Å, $c = 6.95536(1)$ Å. $R_p = 2.78\%$, $wR_p = 3.92\%$, $\chi^2 = 7.787$.

Atom	Site	x	y	z	U_{iso} (x100 Å ²)
Co	4 <i>b</i>	0.5	0	0	0.386(12)
U	4 <i>e</i>	0.032380(27)	0	0.25	1.0314(20)
O(1)	8 <i>i</i>	0.0302(4)	0.29314(35)	0.25	1.49(6)
O(2)	8 <i>h</i>	0.1923(4)	0	-0.02195(33)	0.60(6)

Table S3. Structural parameters for MgUO₄ obtained from refinements in space group *Ibmm* against SC-XRD data recorded at $\lambda = 0.71073 \text{ \AA}$. $a = 6.595(5) \text{ \AA}$, $b = 6.519(5) \text{ \AA}$, $c = 6.923(5) \text{ \AA}$. Final R indexes (all data): $R_1 = 1.07\%$, $wR_2 = 2.35\%$, $\chi^2 = 1.082$.

Atom	Site	x	y	z	U_{eq}^* ($\text{\AA}^2 \times 10^{-2}$)	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg	4 <i>b</i>	0.5	0	0	0.70(3)	0.44(6)	0.78(8)	0.88(8)	0	0.06(5)	0
U	4 <i>e</i>	0.02300(2)	0	0.25	0.423(6)	0.638(9)	0.368(8)	0.263(8)	0	0	0
O1	8 <i>i</i>	0.0240(3)	0.2974(4)	0.25	0.81(4)	1.15(11)	0.51(10)	0.78(10)	-0.03(7)	0	0
O2	8 <i>h</i>	0.1943(4)	0	-0.0170(3)	0.77(4)	0.49(9)	1.15(11)	0.67(10)	0	-0.08(7)	0

* U_{eq} = equivalent isotropic displacement parameters.

Section S2. DFT calculations of AUO₄

Table S4: Results from DFT calculations using the PBEsol functional (and from previous fitting procedure with DFT+*U*).

	method	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	volume [Å ³]	dist. U ⁶⁺ [Å]
β-CdUO ₄	exp. <i>Cmmm</i>	7.02	6.85	3.52	169.3	0.00
	DFT (<i>U</i> = 0)	7.05	6.87	3.50	169.6	0.00
	fitted	7.02	6.85	3.52	169.5	0.00
MnUO ₄	exp. <i>Ibmm</i>	6.75	6.65	6.99	313.7	0.10
	DFT (<i>U</i> = 0)	6.49	6.59	6.89	294.5	0.26
	fitted	6.64	6.54	6.96	302.5	0.16
CoUO ₄	exp. <i>Ibmm</i>	6.50	6.51	6.96	294.0	0.21
	DFT (<i>U</i> = 0)	6.30	6.47	6.82	278.2	0.38
	fitted	6.44	6.39	6.92	285.4	0.22
MgUO ₄	exp. <i>Ibmm</i>	6.60	6.52	6.92	297.6	0.15
	DFT (<i>U</i> = 0)	6.56	6.51	6.88	293.6	0.23
	fitted	6.58	6.47	6.93	294.7	0.09
	fitted (<i>U</i> = 0)	6.54	6.50	6.87	292.1	0.24
β-NiUO ₄	exp. <i>Ibmm</i>	6.38	6.37	6.76	275.1	0.24
	DFT (<i>U</i> = 0)	6.32	6.49	6.73	275.8	0.39
	fitted	6.40	6.39	6.85	280.2	0.23

Table S5: *d*- and *f*-orbital occupations and energy differences (per formula unit) obtained for the considered *Ibmm* structures w.r.t. *Cmmm* structures with the DFT+*U* calculations using atomic orbitals (AO) and Wannier functions (WF) as projectors. E_{Hubb} denotes the Hubbard energy value. The energy differences with subtracting (neglecting) the E_{Hubb} (w/o E_{Hubb}) are also reported.

	A^{2+} <i>d</i> -occupations			U^{6+} <i>f</i> -occupations			ΔE [kJ/mol] w.r.t. <i>Cmmm</i>			
	AO	WF	expected	AO	WF	expected	AO	AO w/o E_{Hubb}	WF	WF w/o E_{Hubb}
MnUO ₄	5.4	4.8	5	4.0	0.2	0	+8.19	-7.39	+1.30	-1.87
CoUO ₄	7.3	6.8	7	4.0	0.3	0	+6.93	-7.41	-4.28	-4.40
MgUO ₄	--	--	0	4.0	0.0	0	+0.99	-0.41	-0.20	-0.20
β -NiUO ₄	8.4	7.9	8	4.0	0.4	0	+6.78	-8.29	-3.18	-4.97

Table S6: Eigenvalues, eigenvector and occupation matrices for Ni and U atoms in NiUO₄ in the DFT+U calculations with atomic orbitals (left column) and Wannier (right column) functions as projectors.

Atomic orbitals	Wannier functions
Ni (spin up)	Ni (spin up)
eigenvalues:	eigenvalues:
0.989 0.996 0.998 0.998 0.999	0.967 0.971 0.985 0.988 0.991
eigenvectors:	eigenvectors:
0.918 0.000 0.065 0.017 0.000 0.000 0.017 0.000 0.000 0.983 0.068 0.000 0.931 0.001 0.000 0.014 0.000 0.004 0.981 0.000 0.000 0.983 0.000 0.000 0.017	0.881 0.000 0.074 0.045 0.000 0.000 0.017 0.000 0.000 0.983 0.036 0.000 0.846 0.119 0.000 0.083 0.000 0.080 0.837 0.000 0.000 0.983 0.000 0.000 0.017
occupations:	occupations:
0.990 -0.000 -0.002 -0.001 0.000 -0.000 0.999 -0.000 0.000 0.000 -0.002 -0.000 0.997 -0.000 0.000 -0.001 0.000 -0.000 0.998 -0.000 0.000 0.000 0.000 -0.000 0.996	0.969 -0.000 -0.003 -0.006 0.000 -0.000 0.991 -0.000 0.000 0.003 -0.003 -0.000 0.985 -0.002 0.000 -0.006 0.000 -0.002 0.986 -0.000 0.000 0.003 0.000 -0.000 0.971
Ni (spin down)	Ni (spin down)
eigenvalues:	eigenvalues:
0.154 0.256 0.994 0.995 0.996	0.004 0.006 0.987 0.990 0.991
eigenvectors:	eigenvectors:
0.000 0.953 0.047 0.000 0.000 0.012 0.000 0.000 0.000 0.988 0.000 0.042 0.894 0.063 0.000 0.000 0.005 0.058 0.937 0.000 0.988 0.000 0.000 0.000 0.012	0.000 0.948 0.043 0.010 0.000 0.012 0.000 0.000 0.000 0.988 0.000 0.043 0.957 0.000 0.000 0.000 0.010 0.000 0.990 0.000 0.988 0.000 0.000 0.000 0.012
occupations:	occupations:

0.291 -0.000 -0.148 -0.051 0.000 -0.000 0.986 -0.000 0.000 0.091 -0.148 -0.000 0.963 -0.011 0.000 -0.051 0.000 -0.011 0.991 -0.000 0.000 0.091 0.000 -0.000 0.164	0.057 -0.000 -0.197 -0.094 -0.000 -0.000 0.980 -0.000 0.000 0.106 -0.197 -0.000 0.945 -0.020 0.000 -0.094 0.000 -0.020 0.981 -0.000 -0.000 0.106 0.000 -0.000 0.015
total occupations (up, down, total):	total occupations (up, down, total):
4.97968 3.39461 8.37429	4.90311 2.97806 7.88117
U (spin up)	U (spin up)
eigenvalues:	eigenvalues:
0.058 0.169 0.258 0.263 0.363 0.413 0.574	0.006 0.013 0.014 0.018 0.028 0.043 0.102
eigenvectors:	eigenvectors:
0.000 0.000 0.000 0.969 0.000 0.031 0.000 0.661 0.000 0.000 0.000 0.000 0.000 0.339 0.000 0.000 0.815 0.000 0.185 0.000 0.000 0.000 0.000 0.000 0.031 0.000 0.969 0.000 0.000 1.000 0.000 0.000 0.000 0.000 0.000 0.339 0.000 0.000 0.000 0.000 0.000 0.661 0.000 0.000 0.185 0.000 0.815 0.000 0.000	0.000 0.000 0.071 0.000 0.000 0.929 0.000 0.450 0.000 0.000 0.000 0.000 0.000 0.550 0.000 0.000 0.000 0.123 0.877 0.000 0.000 0.000 0.000 0.929 0.000 0.000 0.071 0.000 0.000 1.000 0.000 0.000 0.000 0.000 0.000 0.550 0.000 0.000 0.000 0.000 0.000 0.450 0.000 0.000 0.000 0.877 0.123 0.000 0.000
occupations:	occupations:
0.268 -0.000 0.000 0.026 -0.000 0.000 -0.000 -0.000 0.233 -0.000 0.000 0.000 -0.244 -0.000 0.000 -0.000 0.277 0.000 -0.000 -0.000 -0.041 0.026 0.000 0.000 0.408 -0.000 -0.000 -0.000 -0.000 0.000 -0.000 -0.000 0.169 0.000 -0.000 0.000 -0.244 -0.000 -0.000 0.000 0.399 0.000 -0.000 -0.000 -0.041 -0.000 -0.000 0.000 0.343	0.041 -0.000 -0.000 0.008 -0.000 0.000 -0.000 -0.000 0.059 -0.000 0.000 -0.000 -0.048 -0.000 -0.000 -0.000 0.027 -0.000 -0.000 -0.000 -0.003 0.008 0.000 -0.000 0.016 -0.000 -0.000 -0.000 -0.000 -0.000 -0.000 -0.000 0.013 0.000 -0.000 0.000 -0.048 -0.000 -0.000 0.000 0.049 0.000 -0.000 -0.000 -0.003 -0.000 -0.000 0.000 0.020
U (spin down)	U (spin down)
eigenvalues:	eigenvalues:

0.057 0.169 0.213 0.243 0.322 0.385 0.547	0.004 0.007 0.008 0.011 0.023 0.025 0.114
eigenvectors:	eigenvectors:
0.000 0.000 0.000 1.000 0.000 0.000 0.000 0.672 0.000 0.000 0.000 0.000 0.000 0.328 0.000 0.000 0.686 0.000 0.314 0.000 0.000 0.000 0.000 0.000 0.000 0.000 1.000 0.000 0.000 1.000 0.000 0.000 0.000 0.000 0.000 0.328 0.000 0.000 0.000 0.000 0.000 0.672 0.000 0.000 0.314 0.000 0.686 0.000 0.000	0.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000 0.456 0.000 0.000 0.000 0.000 0.544 0.015 0.000 0.000 0.000 0.000 0.985 0.000 0.000 0.000 1.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 1.000 0.000 0.000 0.000 0.000 0.544 0.000 0.000 0.000 0.000 0.456 0.985 0.000 0.000 0.000 0.000 0.015 0.000
occupations:	occupations:
0.243 -0.000 0.000 0.000 -0.000 0.000 -0.000 -0.000 0.218 -0.000 0.000 0.000 -0.230 -0.000 0.000 -0.000 0.247 0.000 -0.000 -0.000 -0.051 0.000 0.000 0.000 0.385 -0.000 -0.000 -0.000 -0.000 0.000 -0.000 -0.000 0.169 0.000 -0.000 0.000 -0.230 -0.000 -0.000 0.000 0.386 0.000 -0.000 -0.000 -0.051 -0.000 -0.000 0.000 0.288	0.023 -0.000 0.000 0.000 -0.000 0.000 -0.000 -0.000 0.065 -0.000 0.000 -0.000 -0.054 -0.000 0.000 -0.000 0.025 0.000 -0.000 -0.000 -0.003 0.000 0.000 0.000 0.008 -0.000 -0.000 0.000 -0.000 -0.000 -0.000 -0.000 0.011 0.000 -0.000 0.000 -0.054 -0.000 -0.000 0.000 0.056 0.000 -0.000 -0.000 -0.003 0.000 -0.000 0.000 0.004
total occupations (up, down, total):	total occupations (up, down, total):
2.09763 1.93723 4.03486	0.22476 0.19087 0.41563

Section S3: Variable Temperature S-XRD Structural Studies of MnUO_4 and CoUO_4

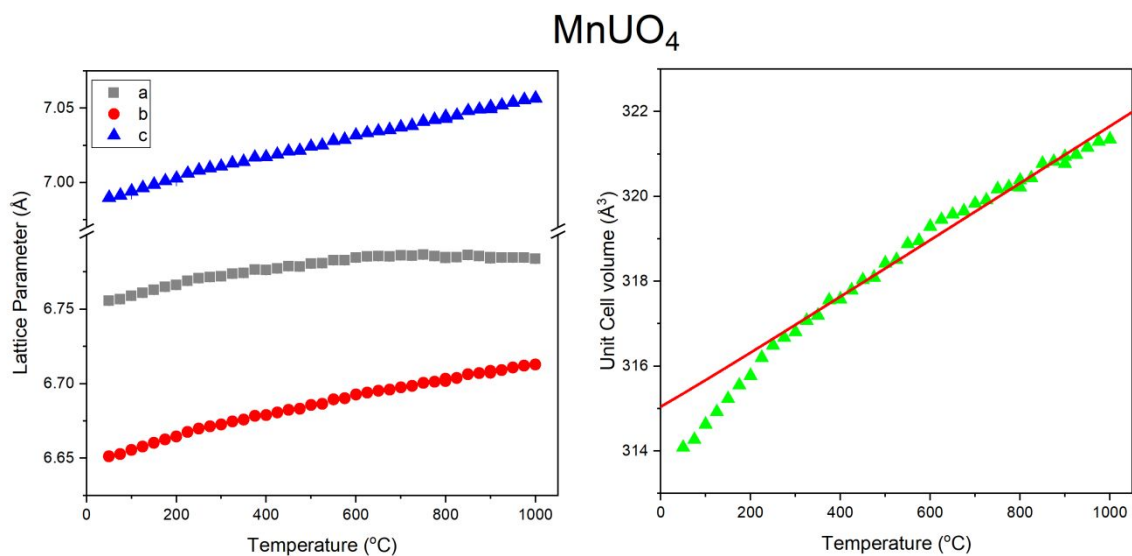


Figure S1: Temperature dependence of the lattice parameters (LHS) and unit cell volume (RHS) for MnUO_4 from 50 to 1000 °C obtained from Rietveld refinements against S-XRD data. The solid line is a linear fit to the HT region (400-1000 °C) and illustrates the reduction in the volume that accompanies the cooperative tilting at temperatures below 200 °C.

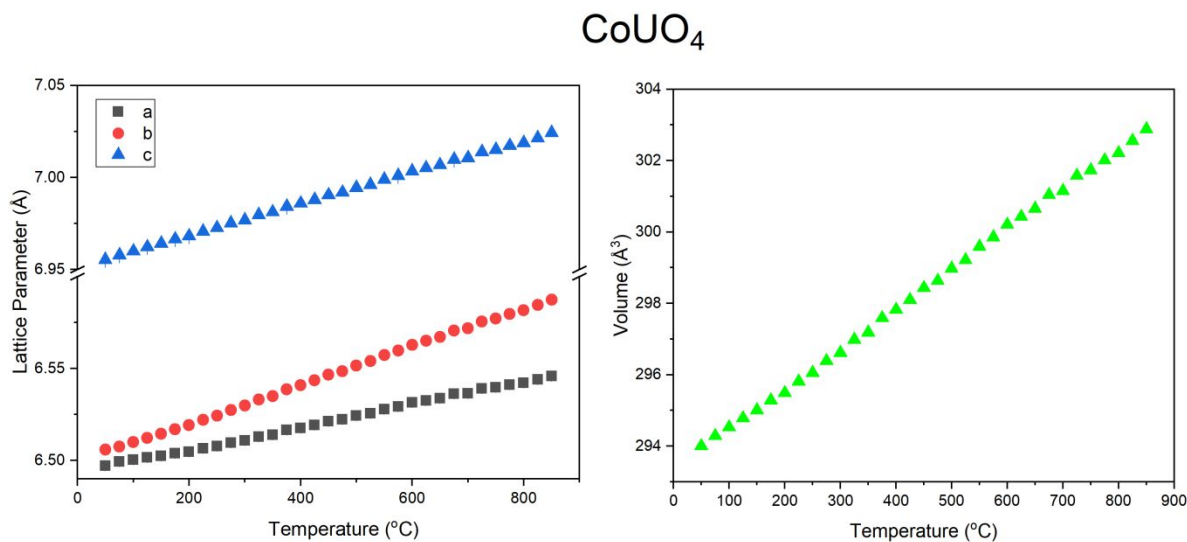


Figure S2: Temperature dependence of the lattice parameters (LHS) and unit cell volume (RHS) for CoUO_4 from 50 to 850 °C obtained from Rietveld refinements against S-XRD data.

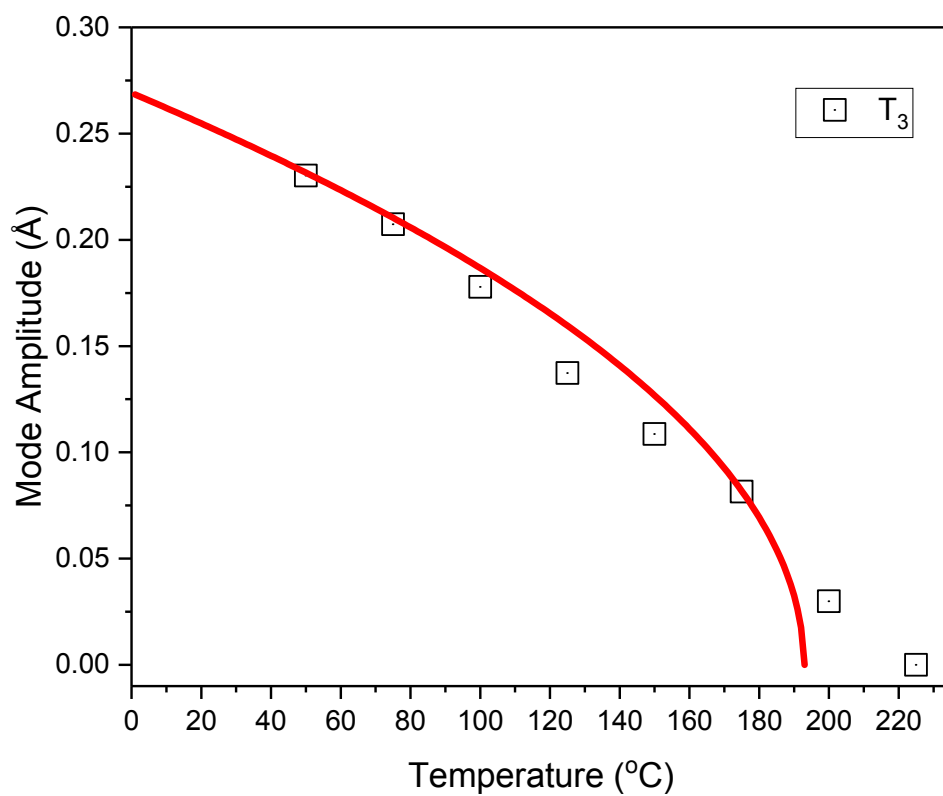


Figure S3. Temperature dependence of the amplitude of the T₃- mode, estimated from the refined structures of MnUO₄. The solid line is a fit to the expression $A = C(T_c - T)^{0.5}$.

Section S4: Room Temperature S-XRD and NPD patterns of β -CdUO₄ Refined in *Cmmm* and *Ibmm*

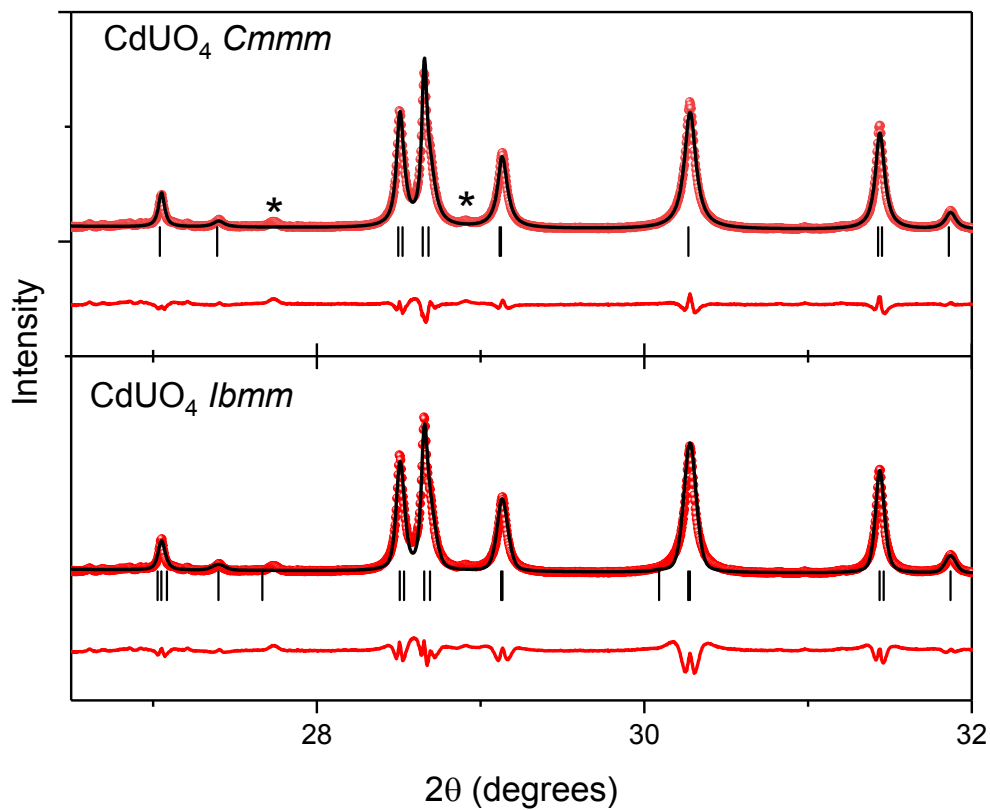


Figure S4a: Portions of the Rietveld fits using S-XRD data for β -CdUO₄ in both *Cmmm* and *Ibmm*, illustrating that the space groups cannot be distinguished by peak extinction alone. Weak peaks from trace amounts of α -CdUO₄ are indicated by *.

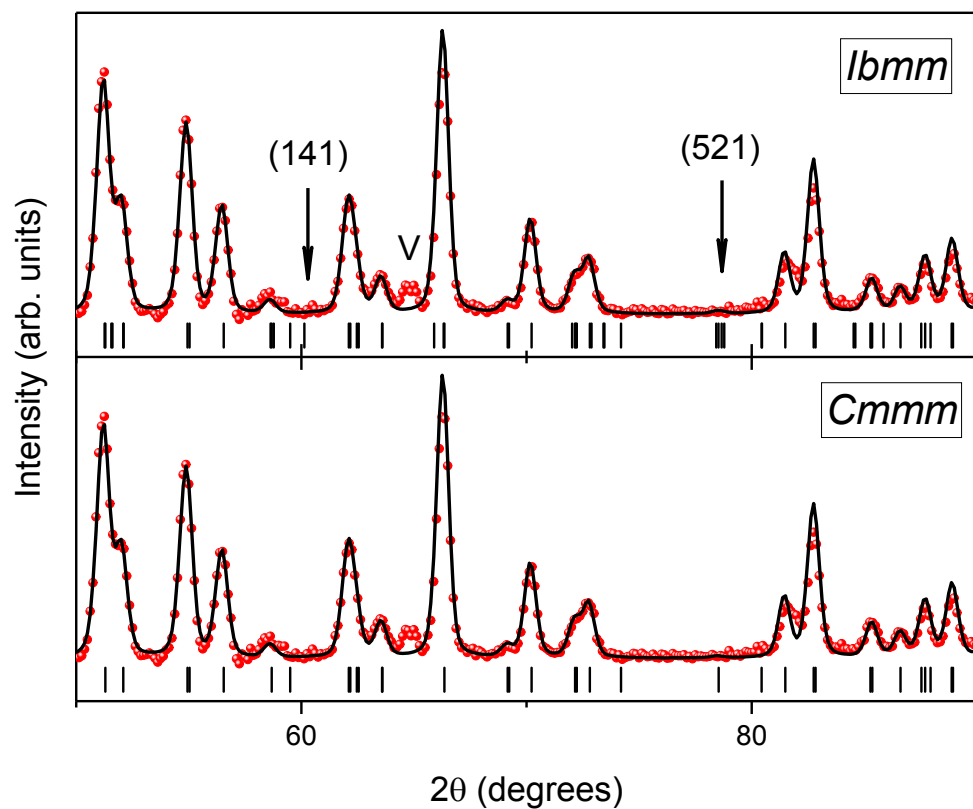


Figure S4b: Portions of the Rietveld fits using NPD data for β -CdUO₄ in both *Cmmm* and *Ibmm*. This figure illustrates the weakness of selected distinguishing reflections. The unfitted peak near 64 degrees is from the Vanadium sample holder.

