

Antiferromagnetism in $M\text{UO}_3$ ($M = \text{Na}, \text{K}, \text{Rb}$) studied by neutron diffraction

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Abstract

Simultaneous refinements of X-ray and neutron powder diffraction patterns taken on the $M\text{UO}_3$ perovskite compounds with $M = \text{Na}, \text{K}$ and Rb , were performed to reveal anisotropy in the temperature factors, mainly of oxygen. No anisotropic thermal motion was found.

The magnetic ordering of the compounds has been investigated with low temperature neutron diffraction. It is found that all these compounds show G-type antiferromagnetic ordering with a similar, orthorhombic magnetic unit cell. The propagation vector could only be determined for the orthorhombic NaUO_3 compound and was found to point in the z -direction. The refined magnetic moment for U^{5+} in these structures was found to be around $0.20(3) \mu_{\text{B}}$.

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1. Introduction

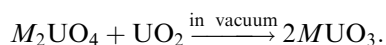
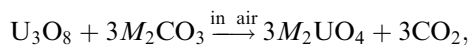
The magnetic and optical properties of the actinide elements have always attracted much attention. The theoretical treatment of systems with $5f$ elements can become extremely complicated because of the comparable magnitudes of the crystal field, the spin–orbit coupling and the electron–electron repulsion interactions. As such, studies of the $M\text{UO}_3$ ($M = \text{alkaline cation}$) series of compounds have been numerous [1–15], because they contain uranium in the U(V) valence state, which has the electronic configuration $[\text{Rn}]5f^1$. This simplifies the situation, because there are no electron–electron repulsions to take into account.

In this paper, the crystallographic and magnetic structures of the $M\text{UO}_3$ compounds with $M = \text{Na}, \text{K}$ and Rb are investigated. The revisiting of this system was triggered by X-ray photoelectron spectroscopy (XPS) results, which indicate the presence of multiple uranium valences in these compounds [16,17], while

their perovskite structures only allow for one uranium position.

2. Experimental and data-analysis

The preparation of these compounds is commonly accomplished through a two-step process, in which the U(VI) uranate $M_2\text{UO}_4$ is first prepared in air and then, after mixing with UO_2 , reduced to $M\text{UO}_3$ [2] in an inert atmosphere or vacuum, which is referred to as the Bartram and Fryxell method



We have taken a one-step route through careful control of the oxygen potential of the furnace atmosphere. Because UO_2 is known to readily deviate from stoichiometry, errors in the weighting of the initial products are introduced, which can produce residual unwanted phases in the end product. This error is avoided by starting from U_3O_8 , which is obtained by

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oxidizing UO_{2+x} in air at 500°C . A stoichiometric mixture of the alkali metal carbonate and U_3O_8 is then treated in a tubular furnace at a temperature of 800°C for 17 h. At that temperature, NaUO_3 is stable at oxygen potentials between roughly -500 and -250 kJ/mol [18]. For the other compounds, the oxygen potential limits are comparable, because their phase diagrams and thermodynamic properties are similar. The oxygen potential in the furnace was controlled using an atmosphere of $\text{Ar} + 5\% \text{H}_2$, humidified to a dew point of 20.8°C , which leads to a $\text{H}_2/\text{H}_2\text{O}$ ratio of about 2 and thus an oxygen potential of about -390 kJ/mol at the temperature of the furnace. This procedure leads to a single-phase powder for all compounds, as was established by X-ray diffraction. No contamination with other phases was found and the powders were well-crystallised.

The X-ray diffraction analyses were carried out using a Philips X'Pert θ - θ diffractometer, equipped with a Cu tube and an X'Celerator solid state area detector. The $\text{CuK}\beta$ contribution is filtered out using a Ni filter and a small antiscatter shield is mounted in front of the detector to reduce the background. Soller slits of 0.04 rad and a fixed divergence slit of $\frac{1}{2}^\circ$ are used. The samples were backloaded to avoid preferential orientation. Scans are made with a step size of $0.0084^\circ 2\theta$ (as dictated by the X'Celerator detector) with 30 s/step for NaUO_3 and RbUO_3 and 100 s/step for KUO_3 .

Room temperature neutron diffraction experiments were carried out at the D1A powder diffractometer at the Institut Laue–Langevin (ILL) in Grenoble. Samples were loaded in a standard vanadium sample container. Diffraction patterns were recorded at wavelengths of 1.39 Å for all compounds. Scans of about 5 h from 10° to $150^\circ 2\theta$ with a step of 0.05° were performed. Additionally, another scan was run at 1.91 Å between 0° and $158^\circ 2\theta$ with a step of 0.05° for NaUO_3 . Magnetic neutron diffraction experiments were performed on the D20 high flux powder diffractometer, using a standard ILL orange cryostat for cooling. The wavelength used there was 2.42 Å and measurements were made between 10° and $150^\circ 2\theta$ with a step of 0.1° . The temperature was cycled between high and low temperature. For NaUO_3 , cycling was between 6 h at 5 K and 6 h at 50 K, for KUO_3 , between 3 h at 3 K and 3 h at 39 K and for RbUO_3 between 3 h at 5 K and 3 h at 50 K.

Data analysis was carried out using the Fullprof Rietveld refinement program [19,20]. The nuclear refinements were performed by simultaneous refinement of the X-ray and D1A neutron diffraction patterns. For the room temperature spectra, the background was refined as a polynomial. The lattice parameters were correlated for both patterns and no preferential orientation was taken into account. The temperature factors are treated anisotropically (as far as allowed by the symmetry of the space group), but only taking into

account the diagonal elements of the matrix. All refinements show full convergence in the final step, with all refinable parameters (57 for NaUO_3 , 38 for KUO_3 and RbUO_3) released.

Due to the very low magnetic contribution to the overall scattering, the refinements of the magnetic structures were done directly on the difference spectra between the low temperature and the high temperature D20 datasets. A constant background was added to these difference spectra in order to exclude all negative data points. After checking that no ferromagnetic contributions existed, the regions of nuclear reflections were excluded from the refinement as the slight change of lattice parameters led to typical down/up spikes in the difference spectra at the positions of nuclear peaks. The nuclear structures (non-magnetic) were refined separately on the low temperature data, in order to determine the scale factor to be used in the refinement of the difference spectra. The scale factor used for the refinement of the magnetic structure can be related to the one found from the purely nuclear refinement through

$$S_m = \left(\frac{V_m}{V_c} \right)^2 \times S_c,$$

where S_m and S_c are the magnetic and crystallographic scale factors and V_m and V_c are the volumes of the magnetic and the crystallographic unit cells.

The magnetic form factor for the U^{5+} ion was calculated in the dipole approximation [21,22]

$$f(Q) = \langle j_0 \rangle + C_2 \times \langle j_2 \rangle \quad (1)$$

in which Q is the momentum transfer $\sin \theta/\lambda$ in Å^{-1} with θ the Bragg angle and λ the neutron wavelength, $\langle j_0 \rangle$ and $\langle j_2 \rangle$ are the Bessel transforms for the single-electron probabilities in the solid and C_2 is related to the ratio of the orbital and the spin contribution to the magnetic moment

$$C_2 = \frac{\mu_L}{\mu_L + \mu_S}, \quad (2)$$

where μ_L and μ_S are the orbital and spin moments for which the total magnetic moment $\mu = \mu_L + \mu_S$. The spin and orbital moments are aligned anti-parallel which can lead to very small total moments. $\langle j_0 \rangle$ and $\langle j_2 \rangle$ were calculated for U^{5+} using the tables of Brown [23].

3. Results

3.1. High resolution data

The MUO_3 uranates have a perovskite structure: KUO_3 and RbUO_3 are regular cubic perovskites (space group $Pm\bar{3}m$), while NaUO_3 is slightly more distorted and orthorhombic (space group $Pbnm$). Combined

refinements of the room temperature X-ray and high resolution neutron data yield the results presented in Tables 1–3 for NaUO₃, KUO₃ and RbUO₃, respectively.

The plots of the neutron and X-ray diffraction patterns of NaUO₃ are displayed in Figs. 1 and 2, showing a good agreement between the calculated and the measured patterns.

3.2. High intensity low temperature data

The difference spectra of the high intensity data revealed the presence of very small additional peaks in the low temperature data sets, as visible in Fig. 3. They were clearly of antiferromagnetic origin and could be indexed on the basis of magnetic unit cells with $a = 5.779 \text{ \AA}$, $b = 5.878 \text{ \AA}$, $c = 8.322 \text{ \AA}$ for NaUO₃, $a = b = 6.079 \text{ \AA}$, $c = 8.597 \text{ \AA}$ for KUO₃ and $a = b = 6.107 \text{ \AA}$, $c = 8.636 \text{ \AA}$ for RbUO₃. Purely nuclear refinements of the low temperature datasets were used to determine these lattice parameters, during which no deviations from the pseudocubic relation $a = b = c/\sqrt{2}$ were found for KUO₃ and RbUO₃.

For the refinement, a magnetic form factor in the dipole approximation (Eq. (1)) was entered for the U⁵⁺ ion. Although the C_2 value can be calculated using the integrated intensities of the magnetic Bragg peaks, the extremely low intensity of the magnetic reflections prevents an adequate estimate of the C_2 value and its associated error in that way. Even though the value of C_2 is therefore not known precisely, the dependence of the spin/orbit ratio on the C_2 parameter is not very high (Eq. (2)). For C_2 varying between 3 and 6, the S/L only varies from 40/60 to 45.5/54.5 (see also Fig. 6). Of course, the magnetic moment values depend on the actual value of C_2 adopted. Refinements with different values for C_2 were performed for all compounds and the results in terms of magnetic moment and R -value are plotted in Figs. 4 and 5.

In the final refinement of the difference spectra the magnetic moment value was the only refinable parameter as we use the lattice constants, width parameters and scale factor from the nuclear refinements of the low

Table 2

Atomic positions, anisotropic Debye–Waller factors, cell parameters and R -factors resulting from the KUO₃ crystal structure refinement

Atom	x/a	y/b	z/c	B_{11} ($\times 10^{-4} \text{ \AA}^2$)	B_{22} ($\times 10^{-4} \text{ \AA}^2$)	B_{33} ($\times 10^{-4} \text{ \AA}^2$)
KUO ₃						
K	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	242(5)	$= B_{11}$	$= B_{11}$
U	0	0	0	137(2)	$= B_{11}$	$= B_{11}$
O	$\frac{1}{2}$	0	0	139(8)	267(5)	$= B_{22}$

Cell parameters: $a = b = c = 4.2930(6) \text{ \AA}$.

$R_{\text{Bragg}}^{\text{neutrons}} = 7.16\%$, $R_{\text{Bragg}}^{\text{X-ray}} = 2.09\%$, $R_{\text{p}}^{\text{neutrons}} = 14.1\%$, $R_{\text{p}}^{\text{X-ray}} = 9.50\%$.

S.G.: $Pm\bar{3}m$ (no. 221); $V = 79.12 \text{ \AA}^3$; $Z = 325.13$.

Table 3

Atomic positions, anisotropic Debye–Waller factors, cell parameters and R -factors resulting from the RbUO₃ crystal structure refinement

Atom	x/a	y/b	z/c	B_{11} ($\times 10^{-4} \text{ \AA}^2$)	B_{22} ($\times 10^{-4} \text{ \AA}^2$)	B_{33} ($\times 10^{-4} \text{ \AA}^2$)
RbUO ₃						
Rb	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	220(5)	$= B_{11}$	$= B_{11}$
U	0	0	0	153(3)	$= B_{11}$	$= B_{11}$
O	$\frac{1}{2}$	0	0	179(16)	211(10)	$= B_{22}$

Cell parameters: $a = b = c = 4.3222(9) \text{ \AA}$.

$R_{\text{Bragg}}^{\text{neutrons}} = 2.79\%$, $R_{\text{Bragg}}^{\text{X-ray}} = 7.04\%$, $R_{\text{p}}^{\text{neutrons}} = 13.5\%$, $R_{\text{p}}^{\text{X-ray}} = 8.77\%$.

S.G.: $Pm\bar{3}m$ (no. 221); $V = 80.74 \text{ \AA}^3$; $Z = 371.49$.

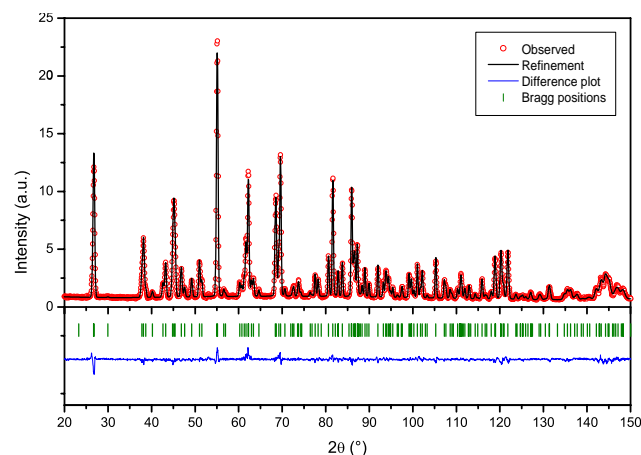


Fig. 1. Room temperature neutron diffraction profile of NaUO₃, compared to the calculated, refined pattern.

Table 1

Atomic positions, anisotropic Debye–Waller factors, cell parameters and R -factors resulting from the NaUO₃ crystal structure refinement

Atom	x/a	y/b	z/c	B_{11} ($\times 10^{-4} \text{ \AA}^2$)	B_{22} ($\times 10^{-4} \text{ \AA}^2$)	B_{33} ($\times 10^{-4} \text{ \AA}^2$)
NaUO ₃						
Na	-0.0075(8)	0.0306(6)	$\frac{1}{4}$	142(11)	152(12)	67(6)
U	$\frac{1}{2}$	0	0	79(2)	75(2)	25(1)
O(1)	0.0959(4)	0.4671(4)	$\frac{1}{4}$	131(8)	146(9)	25(4)
O(2)	0.6982(3)	0.2984(3)	0.0502(2)	108(6)	96(5)	64(3)

Cell parameters: $a = 5.7739(2) \text{ \AA}$, $b = 5.9051(2) \text{ \AA}$, $c = 8.2784(2) \text{ \AA}$.

$R_{\text{Bragg}}^{\text{neutrons}} = 3.64\%$, $R_{\text{Bragg}}^{\text{X-ray}} = 2.94\%$, $R_{\text{p}}^{\text{neutrons}} = 8.21\%$, $R_{\text{p}}^{\text{X-ray}} = 9.61\%$.

S.G.: $Pbnm$ (no. 62); $V = 282.26 \text{ \AA}^3$; $Z = 1236.07$.

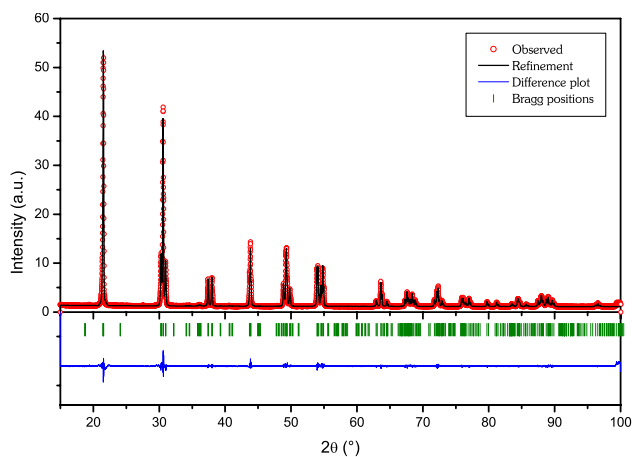


Fig. 2. Room temperature X-ray diffraction profile compared to the calculated, refined pattern of NaUO₃.

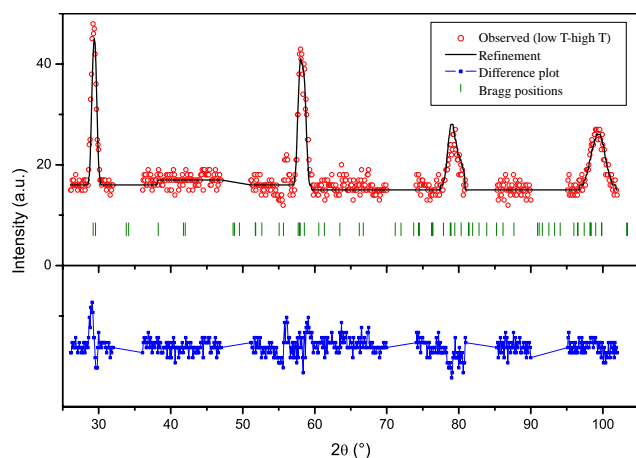


Fig. 3. Difference spectrum of the high (50 K) and low (5 K) temperature high intensity neutron diffraction profiles of NaUO₃, compared to the calculated, refined magnetic pattern.

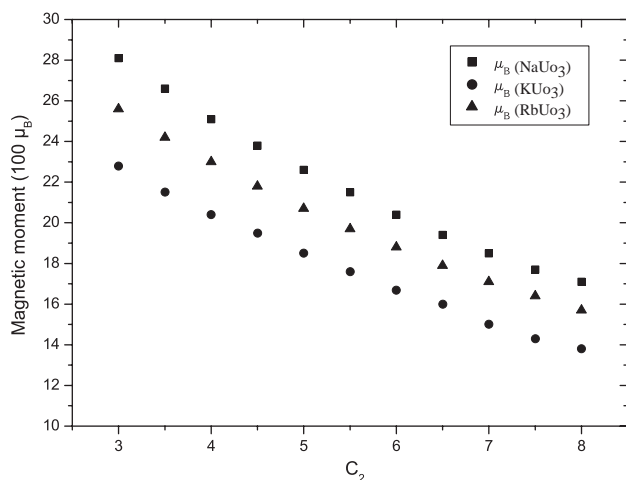


Fig. 4. Magnetic moments found for refinements with different values of C_2 .

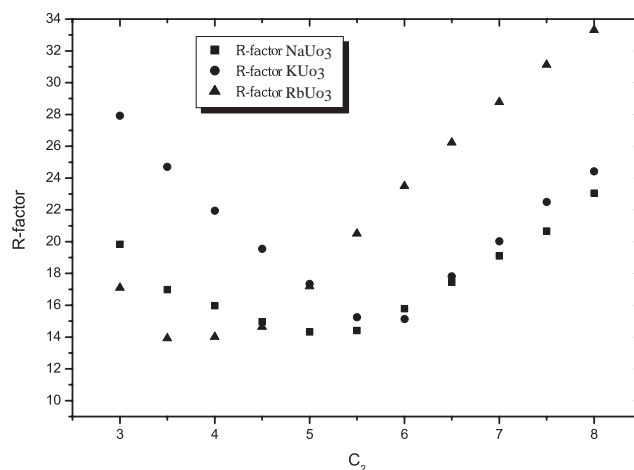


Fig. 5. R -factors resulting from refinements with different values of C_2 .

temperature data. As a result, the errors on the magnetic moment as given by the refinement program are too low. The main source of error lies in the value of C_2 used. Changes in C_2 by ± 1 generate a difference in magnetic moment of around $0.02 \mu_B$ and therefore we conservatively adopt an error of $0.03 \mu_B$ as the error on the refined magnetic moment.

4. Discussion

From literature, recently determined unit cell dimensions for the MUO_3 compounds are $a = 5.779(4) \text{ \AA}$, $b = 5.907(3) \text{ \AA}$, $c = 8.283(4) \text{ \AA}$ for NaUO₃ [10], 4.294 \AA for KUO₃ [13,15] and 4.326 \AA for RbUO₃ [14]. These values are in good agreement with the values determined in this paper. The main interest in the re-determination of the crystal structures was the anisotropy of the temperature factors. The anisotropic temperature factors were refined to investigate the possibility of a breathing mode distortion being present. Such minor modulations were observed for the assumed single-valent perovskite BaBiO₃ and led to the discovery that it was actually better described as a multivalent compound Ba₂Bi³⁺Bi⁵⁺O₆ [24]. However, no appreciable anisotropy is found in the oxygen thermal motion and no significant improvement of the refinement quality is observed comparing refinements performed with isotropic or anisotropic temperature factors. Therefore, single crystal diffraction data would be required to correctly assess the anisotropy of the thermal motion of the oxygen atoms. In any case, the anisotropy seems to be too limited to warrant a description of the MUO_3 compounds as multivalent.

Magnetic susceptibility measurements and electron paramagnetic resonance (EPR) (or electron spin resonance (ESR)) measurements have been performed on

the $M\text{UO}_3$ uranates in the past [1,5–8,10–15]. The results all point to a magnetic ordering at low temperature for these compounds, eg. for NaUO_3 , a sharp spike is found in the magnetic susceptibility at ca. 32 K [5], for KUO_3 a similar spike is found at ca. 16 K [13,15] and for RbUO_3 at 28 K [14].

The magnetic ordering was, however, never observed in neutron diffraction experiments [9,15]. This failure was attributed to the small magnetic moment of the U^{5+} ion, expected to be around $0.66 \mu_B$ (for KUO_3) [15]. This value shows the large influence of the crystal field (octahedral in the perovskite case) on the effective magnetic moment, since the moment for a free f^1 atom (U^{5+}) is calculated at $2.54 \mu_B$ [13].

In this work, the magnetic moments determined for the three compounds are all around $0.20(3) \mu_B$. This value is, even for the D20 as the highest intensity powder diffractometer, at the lower limit of detection. Because of the uncertainties, mainly in the magnetic form factor (value of C_2), due to the extremely low intensity of the magnetic diffraction peaks, we choose to mention only one value for the magnetic moment, instead of different values for each compound. However, in Fig. 4, the reader can find all required data. The individual spin and orbit contributions to this total moment were analysed as a function of the value of C_2 adopted. A graph of these values, as well as the evolution of their ratio with C_2 is shown in Fig. 6. Table 4 shows a (non-exhaustive) overview of experimentally determined U^{5+} effective magnetic moments as they are found in literature. We have found no previous determinations of the magnetic moment of the U^{5+} ion through magnetic refinement of neutron diffraction data. All moments mentioned in Table 4 are based on the temperature variation of the magnetic susceptibility,

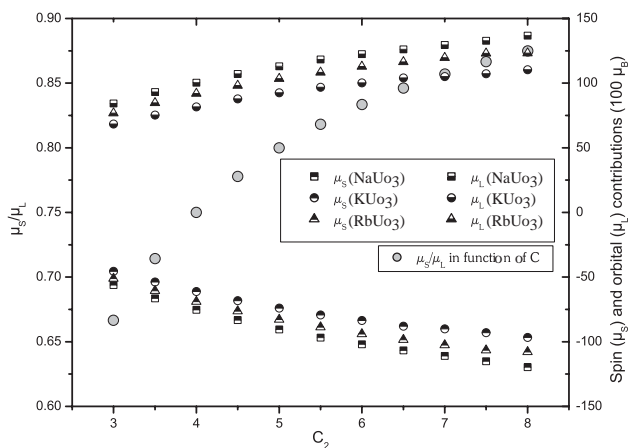


Fig. 6. Individual contributions of orbital and spin magnetic moments to the total magnetic moment for the three compounds studied. Because the two moments have opposite orientation and similar absolute values, the total moment is very small. Also plotted is the evolution of μ_S/μ_L as a function of C_2 . The ratio does not vary a lot with rather important changes in C_2 .

Table 4

Overview of literature data on the experimentally determined effective magnetic moments of U^{5+} in several uranium compounds

Compound	Structure type	μ_{eff} (μ_B)	Reference
NaUO_3	Perovskite	0.62	[8]
KUO_3	Perovskite	0.50	[8]
RbUO_3	Perovskite	0.66	[8]
LiUO_3	Perovskite	0.52	[8]
Li_7UO_6	Perovskite	0.66	[8]
Li_3UO_4	Perovskite	0.56	[8]
Na_3UO_4	Perovskite	0.60	[8]
Li_7UO_6	Perovskite	0.87	[25]
$\text{Ba}_3\text{ZnU}_2\text{O}_9$	Perovskite	0.57	[26]
$\text{Ba}_3\text{CaU}_2\text{O}_9$	Perovskite	1.24 ^a	[27]
$\text{Ba}_3\text{SrU}_2\text{O}_9$	Perovskite	0.56	[27]
Ba_2YUO_6	Perovskite	0.67	[25]
Ba_2ScUO_6	Perovskite	0.49	[25]
BaUO_{3+x}	Perovskite	2.00	[28]
CoU_2O_6	Hexagonal Na_2SiF_6	1.18	[29]
NiU_2O_6	Hexagonal Na_2SiF_6	0.92	[29]
ScUO_4	Fluorite	1.2	[30]
YUO_4	Fluorite	0.9–1.1	[30]
CaU_2O_6	Fluorite	1.3	[30]
CdU_2O_6	Fluorite	1.2	[30]

These moments have been determined through magnetic susceptibility measurements.

^a For this compound the magnetic moment seems to be influenced by a more complex mechanism and cannot be ascribed solely to the U^{5+} ion in an octahedral crystal field.

which is different from our measurements and as such are difficult to compare directly.

The antiferromagnetic ordering is of G-type according to the classification by Wollan and Koehler [31]. A figure of the magnetic structure of NaUO_3 is shown in Fig. 7. As the deviation from pseudocubic symmetry is significant in the case of the Na-compound the magnetic moment direction could be determined and was found to point in the c -direction. At first, it may seem peculiar that the orthorhombic NaUO_3 and the cubic RbUO_3 (and KUO_3) show very similar magnetic unit cells. The arrangement of uranium atoms is the same in both structures and as such it is not entirely surprising to see that they have a similar magnetic structure. There is no evidence of the nuclear structure shifting to another space group, nor of additional ferromagnetism in the nuclear reflections.

5. Conclusion

The crystal structures of the perovskite compounds $M\text{UO}_3$ ($M = \text{Na}, \text{K}, \text{Rb}$) were refined on the basis of high resolution neutron and X-ray data to investigate anisotropy in the temperature factors. No such anisotropy was observed. The crystal structures were found to correspond very well with the literature data.

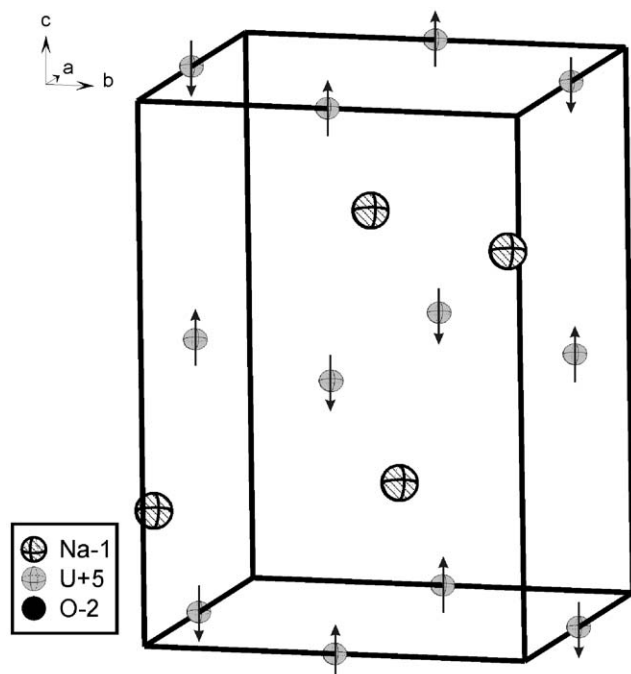


Fig. 7. Magnetic ordering of the U magnetic moments in NaUO_3 in a G-type antiferromagnetic arrangement.

The antiferromagnetic ordering of the same compounds at low temperature was observed by high intensity neutron diffraction. The refinement of the difference spectra of low and high temperature diffraction data, have allowed the determination of the magnetic moment of the U^{5+} ion in these compounds at around $0.20(3) \mu_B$.

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