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A new look at the structural and magnetic properties of potassium neptunate K2NpO4 combining XRD, XANES spectroscopy and low temperature heat capacity

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Physico-chemical properties of potassium neptunate $$\rm K_2NpO_4$$

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Abstract

The physico-chemical properties of the potassium neptunate K_2NpO_4 have been investigated in this work using X-ray diffraction, X-ray Absorption Near Edge Structure (XANES) spectroscopy at the Np-L₃ edge, and low temperature heat capacity measurements. A Rietveld refinement of the crystal structure is reported for the first time. The Np(VI) valence state has been confirmed by the XANES data, and the absorption edge threshold of the XANES spectrum has been correlated to the Mössbauer isomer shift value reported in the literature. The standard entropy and heat capacity of K_2NpO_4 have been derived at 298.15 K from the low temperature heat capacity data. The latter suggest the existence of a magnetic ordering transition around 25.9 K, most probably of the ferromagnetic type.

Keywords: Potassium neptunate, X-ray diffraction, XANES, Calorimetry

1. Introduction

The alkali and alkaline earth ternary oxides of uranium, neptunium and plutonium have attracted interest since the 1960s because of their exciting and intriguing electronic and magnetic properties [1, 2]. In these systems with $[Rn]6d^15f^n$ (uranium and neptunium) and $[Rn]6d^05f^n$ (plutonium) electronic configurations, the 5f valence shell electrons have a large spatial extension and

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are close in energy to the 6d's, making them prone to chemical bonding, by contrast with the 4f electrons of the lanthanides, which are more core-like. This character leads to a wide range of oxidation states, between +3 and +7, and the occurrence of magnetic ordering behaviour. The theoretical description of these systems appears extremely challenging, however, as the crystal field interaction is usually of the same order of magnitude as the spin-orbit coupling interaction and electronic repulsion [3]. The crystal-field interaction cannot be treated as a small perturbation of the electronic energy levels as is done for the $[Xe]4f^n$ rare earths [3]. In the case of $[Rn]5f^1$ and $[Rn]5f^0$ electronic configurations, however, the contribution from electronic repulsion is removed, which simplifies greatly the interpretation.

A number of studies have recently been reported on several sodium actinide phases because of their relevance for the safety assessment of Sodium-cooled Fast Reactors (SFRs) [4–7]. Those studies have revealed intriguing magnetic properties for the α -Na₂Np(VI)O₄ [7] and Na₄Np(VI)O₅ [6] compositions, and have stressed the need to re-evaluate the Np(VI) crystal-field ground state.

The physical and chemical properties of K_2NpO_4 have been investigated in the present work in an attempt to bring new insights into the complex behaviour of Np(VI) phases. Nectoux *et al.* performed Mössbauer spectroscopy and magnetic susceptibility measurements on this phase in 1981 and reported intriguing results [8]. The authors suggested the occurrence of a first order magnetic transition at 19.5(5) K as the Mössbauer spectra showed hyperfine splitting below that temperature, with an associated magnetic hyperfine field of 122 tesla, corresponding to an ordered moment of about 0.6 μ_B . However, their magnetic susceptibility data did not show any sign of an anomaly around 20 K, as could be expected from the Mössbauer results.

Electronic structures can also be probed using X-ray absorption spectroscopy (XAS) [9]. Coupling XAS measurements in the high-energy-resolution fluorescencedetection (HERFD) mode with theoretical calculations using the Anderson impurity model, Butorin *et al.* [9] have recently estimated the crystal field parameters and 5f occupancy in pentavalent NaUO₃ ($[Rn]5f^1$) and hexavalent Pb₃UO₆ ($[Rn]5f^0$), revealing a significant covalent character of the chemical bond. The XAS data available on solid actinide compounds with a valence state higher than (IV) is still very scarce, however, and the relationship between XAS features and electronic density is not fully understood [10].

In this work, we have synthesized K_2NpO_4 and report for the first time a Rietveld refinement of its crystal structure and XANES spectrum collected at the Np-L₃ edge. The relationship between local coordination environment and shape of the XANES spectra is discussed, as well as the correlation between the edge absorption threshold of the neptunium XANES spectra and the isomer shift value measured by ²³⁷Np Mössbauer spectroscopy [8]. Moreover, low temperature heat capacity measurements have been performed to solve the discrepancy regarding the existence of magnetic ordering in this compound.

2. Experimental methods

2.1. Sample preparation and characterization

 K_2NpO_4 and K_2UO_4 were synthesized under oxygen flow and air by reaction between accurately weighted samples of neptunium dioxide (²³⁷NpO₂, ORNL, Oak Ridge) or uranium dioxide (²³⁸UO_{2.10}, JRC-Karlsruhe stocks) and potassium carbonate (K_2CO_3 , >99%, Baker). The stoichiometric mixtures were heated with intermediate regrinding steps at 1093 K for 22 h and 1073 K for 5 h for the neptunium (green color) and uranium (orange color) compounds, respectively. The purity of the obtained materials was analysed by X-ray diffraction. No secondary phases were detected.

The X-ray diffraction measurements were carried out using a Bruker D8 X-ray diffractometer mounted in the Bragg-Brentano configuration with a copper tube (40 kV, 40 mA) and a curved Ge monochromator (1 1 1), and equipped with a LinxEye position sensitive detector. The data were collected by step scanning in the angle range $10^{\circ} \leq 2\theta \leq 120^{\circ}$ over a period of about 8 h. Structural analysis at room temperature was performed by the Rietveld method with the Fullprof2k suite [11].

2.2. XANES

XANES measurements were performed at the Rossendorf BeamLine (ROBL) [12] of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on the K_2NpO_4 material. Small amounts (5-10 mg) of powdered sample were mixed with boron nitride (BN) in an argon-filled alpha glove box, and pressed into pellets for the measurements. The storage ring operating conditions were 6.0 GeV and 170-200 mA. A double crystal monochromater mounted with a Si(111) crystal coupled to collimating and focusing Rh coated mirrors was used.

XANES spectra were collected at room temperature in transmission mode at the Np-L₃ edge. A step size of 0.5 eV was used in the edge region. The energy E_0 of the edge absorption threshold position was taken at the first inflection point of the spectrum by using the first node of the second derivative. The position of the white-line maximum was selected from the first node of the first derivative. Several acquisitions were performed on the same sample and summed up to improve the signal-to-noise ratio. Before averaging the scans, each spectrum was aligned using the XANES spectrum of a metallic yttrium (17038 eV) reference foil located between the second and the third ionization chambers and measured at the same time as the sample. The ATHENA software (Version 0.9.20) [13] was used to remove the background and to normalize the spectra.

2.3. Low temperature heat capacity of $K_2 NpO_4$ and $K_2 UO_4$

Low temperature heat capacity measurements were performed using thermal relaxation calorimetry [14] with a PPMS (Physical Property Measurement System, Quantum Design) instrument at applied magnetic fields B = 0 and 9 T in the temperature ranges T = (2.1 to 298.4) K for K₂NpO₄ and T = (2.0 to 298.4) to 312.4) K for K_2UO_4 , respectively. The measurements were carried out on 22.6(5) mg of K₂NpO₄ material encapsulated in Stycast 2850 FT, and the heat capacity contribution of the Stycast was subtracted from the recorded data. A more detailed description of the experimental procedure, which is particularly well adapted to the study of radioactive materials, was given in [15]. The measurement of K_2UO_4 was done on 33.2(5) mg of material without additional encapsulation in Stycast. The contributions of the sample platform, wires, and grease were deduced by a separate measurement of an addenda curve. Considering the accuracy of the PPMS instrument as estimated by Lashley et al. [14], the reproducibility of the measurements, and the error introduced by the encapsulation procedure in Stycast of the radioactive neptunium material [15], the final uncertainty was estimated at about 1-2 % in the middle range of acquisition (10-100 K), and reaching about 3% at the lowest temperatures and near room temperature. Self-heating effects coming from the radioactive decay of ²³⁷Np were considered, but appeared negligible. The use of Stycast is the main contributor to the uncertainties on the heat capacity and entropy values quoted hereafter. The final uncertainty for the uranium material is estimated at about 1 % from 100 to 300 K, and reaching about 3 % at the lowest temperatures [14].

3. Results and discussion

3.1. Structural refinement

 K_2NpO_4 is isostructural with K_2UO_4 and crystallizes with tetragonal symmetry in space group I4/mmm. The structure of K_2UO_4 was refined recently based on single crystal data [16]. The refined cell parameters obtained in the present study, a=4.3322(3) Å and c=13.1881(13) Å, are in good agreement with the literature [16]. The refined atomic positions are listed in the Supplementary Information. A Rietveld refinement for the K_2NpO_4 phase is reported for the first time in this work (Figure 1). The cell parameters obtained are a=4.2973(4) Å and c=13.144(12) Å. The refined atomic positions are listed in Table 1, and selected bond lengths in Table 2. In this structure, the neptunium cations are sixfold coordinated, and the octahedra are connected by their equatorial vertices, forming sheets in the (ab) plane (Figure 2a). The pentahedrally coordinated potassium cations are located in between the sheets, holding them together. The NpO_6 octahedra show a neptunyl type of coordination, with two short Np-O1 bonds at 1.84(1) Å in the axial direction, and four long Np-O2 bonds at 2.15(1) Å in the equatorial plane (Figure 2b). The presence of a neptunyl configuration is quite common for hexavalent alkali metal actinide oxide phases. It has been reported already for α -Na₂NpO₄ [7], β -Na₂NpO₄ [17] (orthorhombic in space groups Pbam and Pbca, respectively), and $BaNpO_4$ [18] (orthorhombic in space groups Pbcm). The unit cell volume in K_2NpO_4 (242.7 Å^3) is smaller than for $K_2 UO_4$ (247.5 Å³), which can be related to the decreasing ionic radius along the series of the actinide elements.



Figure 1: Comparison between the observed $(Y_{obs}, \text{ in red})$ and calculated $(Y_{calc}, \text{ in black})$ X-ray diffraction pattern of K₂NpO₄. $Y_{obs} - Y_{calc}$, in blue, is the difference between the experimental and calculated intensities. The Bragg reflections' angular positions are marked in green. The inset shows a zoom of the refinement in the angle range $2\theta = (20\text{-}120^\circ)$. Measurement at $\lambda = \text{Cu-K}\alpha 1$ Å.

Table 1: Refined atomic positions in K₂NpO₄ derived from the analysis of the X-ray diffraction data. $R_{wp} = 13.5$, $R_{exp} = 5.37$, $\chi^2 = 6.29$.

| Atom | Ox. State | Wyckoff | x | y | z | B_0 (Å ²) |
|------|-----------|---------------|-----|-----|-----------|-------------------------|
| Np | +6 | $2\mathrm{a}$ | 0 | 0 | 0 | 0.78(1) |
| Κ | +1 | $4\mathrm{e}$ | 0.5 | 0.5 | 0.1520(2) | 1.91(6) |
| 01 | -2 | $4\mathrm{e}$ | 0 | 0 | 0.1415(5) | 1.5(2) |
| O2 | -2 | 4c | 0.5 | 0 | 0 | 2.1(2) |

Table 2: Selected bond lengths in M_2AnO_4 (An=U,Np; M=Na,K). N is the number of atoms in each coordination shell.

| | | $\mathbf{K}_2 \mathbf{UO}_4$ | $\mathbf{K}_{2}\mathbf{NpO}_{4}$ | α -Na ₂ NpO ₄ |
|-------|--------------|----------------------------------|---------------------------------------|--|
| Bond | \mathbf{N} | ${\bf Bond \ length}({\rm \AA})$ | ${\bf Bond} {\rm length}({\rm \AA})$ | ${\rm Bond}{\rm length}({\rm \AA})$ |
| An-O1 | 2 | 1.809(7) | 1.860(7) | 1.762(5) |
| An-O2 | 4 | 2.166(7) | 2.149(7) | 2.086(5) |
| K-01 | 1 | 2.804(8) | 2.714(8) | |
| K-O2 | 4 | 2.935(2) | 2.934(2) | |



Figure 2: (a) Crystal structure of K_2NpO_4 (K atoms in purple, O atoms in red, NpO_6 octahedra in gray) showing the sheets of corner-sharing NpO_6 octahedra in the (*ab*) plane. (b) NpO_6 octahedron in K_2NpO_4 with the neptunyl type of coordination.

3.2. XANES

The XANES spectrum of K_2NpO_4 collected at the Np-L₃ edge is shown in Figure 3 together with Na₃Np(V)O₄, α -Na₂Np(VI)O₄, and Na₅Np(VII)O₆ reference materials [10]. The valence states of the sodium neptunates were confirmed by ²³⁷Np Mössbauer spectroscopy from the values of their isomer shifts [5–7], while the corresponding XANES spectra were reported by [10]. Further details on the local structural environments and shape of the XANES spectra can be found in the latter publication [10].

The inflection point position of K_2NpO_4 , corresponding to the absorption edge threshold E_0 for the $(2p\rightarrow 6d)$ transitions, is well aligned with that of α -Na₂Np(VI)O₄ (Table 3). These results confirm that neptunium is exclusively in the oxidation state (VI) in K_2NpO_4 , corresponding to a $[Rn]5f^1$ electronic configuration. The Np ion in this structure is therefore a Kramers ion with a ${}^2F_{5/2}$ ground state manifold, and a ${}^2F_{7/2}$ first excited state arising from spinorbit coupling.

Smith *et al.* reported a linear correlation of the absorption edge threshold E_0 determined by XANES versus the Mössbauer isomer shift for the series of sodium neptunates [10]. The value for K₂NpO₄ fits very well with this trend (Figure 4) when using the isomer shift value determined by Nectoux *et al.*, i.e., $\delta_{IS} = -56.9(6) \text{ mm} \cdot \text{s}^{-1}$ at 4.2 K relative to the standard NpAl₂ absorber [8]. The linear variation between E_0 and δ_{IS} can be understood from the fact that both quantities result from the Coulomb interaction with the surrounding electrons. The 5f shells produce a shielding effect on the electronic charge density of the $s_{1/2}$ and $p_{1/2}$ inner shells, which affects the isomer shift: $\delta_{IS} = \alpha \cdot \Delta \rho_e(0)$ (α being a calibration constant and $\Delta \rho_e(0)$ the difference in electronic charge density between the source material and the absorber at the nuclear origin). $\rho_e(0)$ increases with the removal of 5f electrons. Moreover, the increase in formal valence state produces a decrease in Coulomb energy in the final state between the 5f and 6d electrons and the $2p_{3/2}$ core hole [19–21], which leads to



Figure 3: Normalised XANES spectra of K_2NpO_4 (present work) together with NpO_2 , Na_3NpO_4 , α -Na₂NpO₄ and Na₅NpO₆ reference materials [10].

a shift to higher energy of the absorption edge threshold E_0 .

In addition, the XANES spectrum of K_2NpO_4 shows the typical doublepeaked white lines (WL) of Np(V), Np(VI) and Np(VII) compounds [10, 19, 20], while the tetravalent Np(IV)O₂ compound exhibits a single WL peak. The double-peak consists of the main white line at 17620.2(5) eV, and a shoulder and reduced peak amplitude about 15 eV above the Np edge. This feature has traditionally been attributed to localized multiple-scattering resonance of the neptunyl configuration. However, the studies of [10] have shown that the correlation between the shape of the XANES spectra and the local coordination geometries is probably more intricate. The isostructural compounds α -Na₂U(VI)O₄ and α -Na₂Np(VI)O₄, presenting a neptunyl type of configuration, do not show the expected secondary shoulder and reduced peak amplitude, whereas Na₄U(VI)O₅ presenting a "reverse" neptunyl type of configuration does [10]. Other factors could play a role, and effects of the degree of localization of the 5f electrons [10] and core-ionized final states with different 5f occupancies [19, 20] have been suggested.

The absorption edge threshold E_0 is finally slightly higher (0.3 eV) for K_2NpO_4 than for α -Na₂Np(VI)O₄, which could be related to the neptunyl bond distances (Table 2), degree of covalency, or in other words degree of localisation of the 5*f* electrons in both compounds. The shorter the Np-O bonds, the more localized the 5*f* electrons are, and the greater is the Coulomb energy, making it easier to eject an electron from the $2p_{3/2}$ core-shell. However, it is not possible to conclude definitively given the experimental uncertainties (0.5 eV) of the measurements at the Np-L₃ edge, and this would require to perform high-energy-resolution fluorescence detected (HERFD) XANES measurements



Figure 4: Absorption edge threshold E_0 relative to NpO₂ versus isomer shift measured by Mössbauer spectroscopy.

at the M_4 edge.

Table 3: Energies of the inflection points and white lines of the Np-L₃ XANES spectra. The secondary white line, if present, is listed in italics.

| Compound | Inflection point (eV) | White line (eV) | Ref. |
|--|-----------------------|-------------------------|-----------|
| K_2NpO_4 | 17614.5(5) | 17620.2(5) $17631.5(5)$ | This work |
| $Np(IV)O_2$ | 17612.1(5) | 17618.3(5) | [10] |
| $Na_3Np(V)O_4$ | 17613.4(5) | 17618.5(5) | [10] |
| α -Na ₂ Np(VI)O ₄ | 17614.2(5) | 17624.3(5) | [10] |
| $Na_5Np(VII)O_6$ | 17615.1(5) | 17619.0(5) 17626.9(5) | [10] |

3.3. Heat capacity measurements

The heat capacity data of K_2NpO_4 and K_2UO_4 measured at low temperatures in the absence of a magnetic field are shown in Figure 5, and listed in Table 5 and 6 of the Appendix. The two curves cross above T = 150 K, although one would expect them to become equal, corresponding to the same lattice contribution at high temperatures for the uranium and neptunium compounds. But this discrepancy can be related on the one hand to the uncertainty on our experimental results which increases towards high temperatures using the PPMS technique, and on the other hand to the correction for the Stycast contribution. The heat capacities reach values that are about 17-24 J·K⁻¹·mol⁻¹ below the classical Dulong-Petit limit ($C_{lat} = 21R \approx 174.6$ J·K⁻¹·mol⁻¹ for the seven atoms in the formula unit) as the temperature approaches 298.15 K.

The collected data for K_2NpO_4 show a small anomaly at T = 25.9 K, which is almost unaffected by the application of a 9 T magnetic field apart from a small decrease of the amplitude. This feature could be interpreted at first as an indication of the presence of NpO_2 impurity within the investigated material. Indeed, neptunium dioxide shows a sharp λ -anomaly at T = 25.7 K [22, 23] due to rank-5 triakontadipolar order as described in the studies of Santini et al. [24], with a similar behaviour upon application of a magnetic field. However, the X-ray diffraction data did not reveal any secondary NpO₂ phase. Moreover, the shape of the anomaly in K_2NpO_4 does not match that of NpO_2 , although the critical temperatures are very close. The anomaly is very symmetrical in K_2NpO_4 , by contrast with NpO_2 showing an asymmetrical profile. Based on its amplitude, the amount of NpO₂ impurity would correspond to $(26.9 \pm 1.0)\%$, which could be detected easily by the X-rays. We conclude that the anomaly is an intrinsic property of K₂NpO₄. The corresponding magnetic contribution was derived as $S_{mag} = (3.1 \pm 0.1) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ after subtraction of the lattice heat capacity contribution (Figure 7). The latter was approximated with the heat capacity of K_2UO_4 [25] (which has electronic configuration [Rn]5 f^0), as the two compounds are isostructural and have very similar atomic masses. The derived magnetic entropy value represents about 53.8% of the expected orderdisorder entropy for such a Kramers system ($S_{mag} = Rln2$). It is worth pointing out that a similarly low magnetic entropy, i.e. 0.19Rln2, has been reported for α -Na₂NpO₄ [7]



Figure 5: Heat capacity of K_2NpO_4 (\bigcirc) and K_2UO_4 (\Box) measured in zero magnetic field and the numerical fit to the neptunium data (red line).

Interestingly, no anomaly was observed around 19.5(5) K, as could be expected from the Mössbauer results of Nectoux *et al.* [8]. An X-ray diffraction



Figure 6: C_p/T for K_2NpO_4 (\bigcirc) and K_2UO_4 (\Box) measured in zero magnetic field and the numerical fit to the neptunium data (red line).



Figure 7: Electronic contribution to the heat capacity in K_2NpO_4 obtained by subtracting the data for K_2UO_4 [25].

pattern collected after the low temperature heat capacity measurement moreover confirmed that the sample had retained its integrity during the experiment. Since the magnetic susceptibility measurements of the authors also did not show any anomaly around 20 K [8], the existence of a first-order magnetic phase transition at the latter temperature is unlikely. To explain the origin of the magnetic hyperfine splitting reported below 19.5(5) K, we could suggest the occurrence of slow electron spin relaxation phenomenon in this paramagnetic system [26]. However, this is doubtful as it would require a sudden collapse of the relaxation time at the critical temperature. The cell parameters reported by [8] for K_2NpO_4 (a=4.26 Å and c=13.01 Å) are lower than found in this study. A contamination of their sample with a magnetic impurity is possible although unlikely as they reported a single phase material, but they give very little detail on phase preparation and purity. The magnetic hyperfine splitting effect observed by the authors must probably corresponds to the anomaly observed herein at 25.9 K, with a somewhat lower critical temperature. It should be pointed out that differences in critical temperatures of about 3-8 K have been reported in the literature between Mössbauer and magnetic susceptibility results of the uranium-neptunium mixed oxides $U_{1-x}Np_xO_2$ [27]. As for the magnetic susceptibility results of Nectoux et al., a clear deviation from the Curie-Weiss law is observed below about 40 K, which could suggest ferromagnetic ordering below the latter temperature. The hypothesis of a ferromagnetic transition is moreover in good agreement with the low temperature heat capacity data showing a slight decrease of the anomaly at T = 25.9 K upon application of a magnetic field. The negative value of the Curie constant, i.e., $\theta_P = -150$ K, derived from the Curie-Weiss analysis of the data [8] is rather surprising, however. It suggests a more complex order, possibly with a canting of the ferromagnetically coupled moments or with strong antiferromagnetic interactions.

In the present work, the thermodynamic functions of K_2NpO_4 and K_2UO_4 were derived at 298.15 K by fitting the experimental data to theoretical functions below T = 8.0 K and T = 20.0 K [28], respectively, and a combination of Debye and Einstein heat capacity functions [29–31] from T = (7.8 to 298.4) K and from T = (20.0 to 312.4) K, respectively. The fitted data are shown with solid and dotted lines in Figures 5 and 6. The heat capacity values at 298.15 K were obtained by interpolation, yielding $C_{p,m}^{o}(K_2NpO_4, cr, 298.15K) = (152.7\pm4.5)^1$ $J\cdot K^{-1} \cdot mol^{-1}$ and $C_{p,m}^{o}(K_2UO_4, cr, 298.15K) = (156.5\pm4.7)^2 J\cdot K^{-1} \cdot mol^{-1}$. The experimental standard entropies at 298.15 K were determined by numerical integration of $(C_{p,m}/T) = f(T)$ using the aforementioned fitted functions, and including the magnetic entropy contribution, yielding $S_m^o(K_2NpO_4, cr, 298.15K) =$ (209.3 ± 4.9) $J\cdot K^{-1} \cdot mol^{-1}$ and $S_m^o(K_2UO_4, cr, 298.15K) = (210.1\pm2.7)$ $J\cdot K^{-1} \cdot mol^{-1}$, respectively. The values obtained for K_2NpO_4 are slightly lower than that of K_2UO_4 , whereas the inverse behaviour would be expected. However this is due to the uncertainty introduced by the use of Stycast as mentionned before and

¹The quoted uncertainty corresponds to the standard uncertainty.

 $^{^2\}mathrm{The}$ quoted uncertainty corresponds to the standard uncertainty.

the crossing of the two curves. When adding the derived magnetic entropy to the lattice contribution of K_2UO_4 , one derives 213.2 J·K⁻¹·mol⁻¹ for the standard entropy of K_2NpO_4 , which remains within the uncertainty of the present measurement.

3.3.1. Fitting of the lattice contribution above $T = 8.0 \text{ K} (K_2 N p O_4)$ and $T = 20.0 \text{ K} (K_2 U O_4)$.

At very low temperatures where the thermal expansion is negligible, the heat capacity at constant pressure can be approximated to the heat capacity at constant volume $C_{\rm p,m} \approx C_{\rm V,m}$, which comprises lattice vibrations, electronic, and magnetic contributions [32]

The lattice contribution dominates at temperatures above about T = (8-20) K, and can be modelled using a combination of Debye and Einstein functions, as written in equation (1). Two Einstein functions were used in this work to fit the data. Fitting with a single Einstein function was attempted, but could not reproduce accurately the high temperature region.

$$C_{p,m} = n_D D(\theta_D) + n_{E1} E(\theta_{E1}) + n_{E2} E(\theta_{E2})$$
(1)

where R is the universal gas constant equal to 8.3144621 J·K⁻¹·mol⁻¹, $D(\theta_D)$, $E(\theta_{E1})$, and $E(\theta_{E2})$ are the Debye and Einstein functions, respectively, as written in equations (2) and (3). θ_D , θ_{E1} , and θ_{E2} are the characteristic Debye and Einstein temperatures. n_D , n_{E1} , and n_{E2} are adjustable parameters, whose sum $(n_D + n_{E1} + n_{E2})$ should be approximately equal to the number of atoms in the formula unit (i.e., 7 in this case).

$$D(\theta_D) = 9R(\frac{1}{x})^3 \int_0^x \frac{e^x x^4}{[e^x - 1]^2} \cdot dx, \quad x = \frac{\theta_D}{T}$$
(2)

$$E(\theta_E) = 3Rx^2 \frac{e^x}{[e^x - 1]^2}, \quad x = \frac{\theta_E}{T}$$
(3)

The fitted parameters are listed in Table 4. The sum $(n_D + n_{E1} + n_{E2})$ is very close to 7.

3.4. Fitting below $T = 8.0 K (K_2 N p O_4)$ and $T = 20.0 K (K_2 U O_4)$.

At very low temperatures (T < 20 K), the phonon contribution is well-represented using an harmonic-lattice model [28], as expressed by the polynomial function (4), where the number of required terms augments with the high temperature limit of the fit:

$$C_{latt} = \sum B_n T^n$$
, where $n = 3, 5, 7, 9, 11..$ (4)

The electronic contribution of the conduction electrons at the Fermi surface are represented with a linear term γT [33]. For insulating materials such as

| $\mathbf{K}_{2}\mathbf{NpO}_{4}$ | | | | | | | | |
|--------------------------------------|---------------|--|---------------------------|--|--|--|--|--|
| Debye and Einst | tein fit | Harmonic lattice-model | | | | | | |
| Temp. range/K | 7.7.1 - 298.4 | Temp. range/K | 2.1-8.0 | | | | | |
| $n_D/{ m mol}$ | 2.3637 | $\delta/{f mJ}{f \cdot}{f mol}^{-1}{f \cdot}{f K}^{-1}$ | 22.25 | | | | | |
| $	heta_D/{f K}$ | 154.41 | $B_3/{ m mJ}{\cdot}{ m mol}^{-1}{\cdot}{ m K}^{-4}$ | $-5.00553 \cdot 10^{-1}$ | | | | | |
| $n_{E1}/{f mol}$ | 1.9806 | $B_5/{ m mJ}{\cdot}{ m mol}^{-1}{\cdot}{ m K}^{-6}$ | $6.48526 \cdot 10^{-2}$ | | | | | |
| $	heta_{E1}/{f K}$ | 588.19 | $B_7/{ m mJ}{\cdot}{ m mol}^{-1}{\cdot}{ m K}^{-8}$ | $-1.13475 \cdot 10^{-3}$ | | | | | |
| n_{E2}/\mathbf{mol} | 2.5292 | $B_9/\mathrm{mJ}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-10}$ | $7.32029 \cdot 10^{-6}$ | | | | | |
| $	heta_{E2}/{f K}$ | 287.56 | | | | | | | |
| $n_D + n_{E1} + n_{E2}/\mathbf{mol}$ | 6.87 | | | | | | | |
| $\mathbf{K}_{2}\mathbf{UO}_{4}$ | | | | | | | | |
| Debye and Einst | tein fit | Harmonic lattice-model | | | | | | |
| Temp. range/K | 19.8 - 312.4 | Temp. range/K | 2.0 - 20.3 | | | | | |
| $n_D/{ m mol}$ | 2.0522 | $\delta/\mathbf{mJ}\cdot\mathbf{mol}^{-1}\cdot\mathbf{K}^{-1}$ | | | | | | |
| $	heta_D/{f K}$ | 157.08 | $B_3/{ m mJ}{\cdot}{ m mol}^{-1}{\cdot}{ m K}^{-4}$ | $6.43253 \cdot 10^{-1}$ | | | | | |
| n_{E1}/\mathbf{mol} | 2.8798 | $B_5/{ m mJ}{\cdot}{ m mol}^{-1}{\cdot}{ m K}^{-6}$ | $7.77235 \cdot 10^{-3}$ | | | | | |
| $	heta_{E1}/{f K}$ | 256.28 | $B_7/{ m mJ}{\cdot}{ m mol}^{-1}{\cdot}{ m K}^{-8}$ | $-4.50504 \cdot 10^{-5}$ | | | | | |
| $n_{E2}/{f mol}$ | 2.1601 | $B_9/{ m mJ}{\cdot}{ m mol}^{-1}{\cdot}{ m K}^{-10}$ | $1.03519 \cdot 10^{-7}$ | | | | | |
| $	heta_{E2}/{f K}$ | 610.54 | $B_{11}/{ m mJ}{\cdot}{ m mol}^{-1}{\cdot}{ m K}^{-12}$ | $-8.70422 \cdot 10^{-11}$ | | | | | |
| | | | | | | | | |
| $n_D + n_{E1} + n_{E2}/\mathbf{mol}$ | 7.09 | | | | | | | |

Table 4: Summary of fitting parameters of the heat capacity of K_2NpO_4 and K_2UO_4 .

 K_2NpO_4 and K_2UO_4 , the electronic specific heat is zero. However, a linear term was reported in materials such as α -FeOOH [28], Fe₃(P₂O₇)₂ [34], and Sr₂TiSi₂O₈ [35], which was related to departure from stoichiometry, oxygen vacancies or defects within the material [28].

The heat capacity of K_2NpO_4 was fitted with the harmonic model using four terms over the temperature range T = (2.1 to 8.0) K. That of $K_2 UO_4$ was fitted with five terms over the temperature range T = (2.0 to 20.3) K. The corresponding coefficients are listed in Table 4. In addition, the use of a linear δT term appeared necessary to describe the experimental curve of K₂NpO₄. More recently, the occurrence of such linear term was also reported in Na₄NpO₅ [36], which was related to the presence of defects within the material and an asymmetric peak profile shape in opposite directions for successive hkl reflections clearly visible on the X-ray diffraction pattern. The X-ray diffraction data of K₂NpO₄ does not show such features, however. Self-heating effects coming from the radioactive decay of ²³⁷Np were considered, but appeared negligible. Moreover, departure from stoichiometry is unlikely according to the present Np-L₃ XANES results, and Mössbauer data of [8]. Hence, the physical origin of this feature remains unclear. The appearance of a nuclear Schottky effect arising from the magnetic hyperfine splitting interaction between the unpaired 5f electron and the magnetic moment at the Np nucleus (I=5/2) was suggested for Na_2NpO_4 as the corresponding data showed a re-increase below 3.7 K [37]. K_2NpO_4 might show similar behaviour (Figure 7), but we cannot conclude in the absence of data below 2.0 K, which would require complementary measurements using a ³He refrigerator.

4. Conclusion

A Rietveld refinement of the crystal structure of K_2NpO_4 , tetragonal in space group I4/mmm, is reported for the first time in the present work. The refined cell parameters and bond lengths are in good agreement with the trend of decreasing ionic radii along the actinide series. XANES data have also been collected at the Np-L₃ edge, which have confirmed the hexavalent state of neptunium in this compound, and therefore the assigned stoichiometry. The measured absorption edge threshold E_0 fits very well the linear correlation observed for the sodium neptunates between E_0 and the isomer shift value δ_{IS} measured by Mössbauer spectroscopy. Moreover, double peak white lines have been observed for K_2NpO_4 , which are usually attributed to multiple scattering resonance of the actinyl compounds, but the interpretation could be more intricate. Electronic density calculations are needed to bring more insight into those complex features.

Low temperature heat capacity data have been collected in the temperature range T = (2.1 to 298.4) K for K_2NpO_4 and T = (2.0 to 312.4) K for K_2UO_4 , and the standard entropy and heat capacity of both compounds have been derived at 298.15 K. The latter data have revealed the presence of an anomaly at 25.9 K with an associated magnetic entropy $S_{mag} = (3.1 \pm 0.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}$ $^{-1}$, which most probably corresponds to the magnetic hyperfine splitting event observed in the literature by Mössbauer spectroscopy at a slightly lower temperature, i.e., T = 19.5(5) K) [8]. Both the present low temperature heat capacity data and the magnetic susceptibility measurements of Nectoux et al. [8] are consistent with the hypothesis of a ferromagnetic ordering transition around T =26 K. Complementary studies involving repeated Mössbauer spectroscopy and magnetic susceptibility measurements, as well as neutron diffraction measurements on a well-characterized material, would allow to confirm those results. Finally, the amplitude of the anomaly at 25.9 K is smaller than expected for this Kramers system $(S_{mag} = \text{Rln2})$, but similar results have also been reported for α -Na₂NpO₄. The low values of the ordered moment derived from the Mössbauer data ($\sim 0.6 \mu_B$), of the paramagnetic effective moment derived from the magnetic susceptibility data ($\mu_{eff}=1.37 \ \mu_B$), and of the magnetic entropy $(S_{mag} = 0.538 \text{Rln2})$, are not unusual for $5f^1$ systems. Further investigations involving spectroscopy measurements at low energy and theoretical calculations are clearly required to get further insight into the Np(VI) crystal-field ground state and magnetic behaviour of the alkali and alkaline-earth neptunates.

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Appendices

| Т | $C^{\mathbf{o}}$ | Т | $C^{\mathbf{o}}$ | Т | C^{o} | Т | C° |
|------------------|--|----------------|--|----------------|--|------------------|--|
| (\overline{K}) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ | (K) | $(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})$ | (K) | $(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})$ | (\overline{K}) | $(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})$ |
| 298.43 | 150.54 | 85.02 | 78.554 | 24.42 | 15.844 | 6.48 | 0.34949 |
| 294.03 | 150.86 | 83.99 | 77.755 | 23.85 | 14.756 | 6.37 | 0.33499 |
| 289.93 | 150.33 | 82.96 | 76.911 | 23.36 | 13.900 | 6.28 | 0.32159 |
| 285.82 | 149.69 | 81.93 | 76.129 | 22.84 | 12.998 | 6.18 | 0.30762 |
| 281.73 | 149.58 | 80.89 | 75.293 | 22.31 | 12.091 | 6.08 | 0.29390 |
| 277.63 | 149.82 | 79.86 | 74.402 | 21.78 | 11.282 | 5.99 | 0.28239 |
| 273.52 | 149.74 | 78.83 | 73.565 | 21.27 | 10.562 | 5.89 | 0.27128 |
| 269.43 | 149.51 | 77.80 | 72.677 | 20.75 | 9.8837 | 5.80 | 0.26038 |
| 265.33 | 149.08 | 76.76 | 71.782 | 20.23 | 9.2323 | 5.71 | 0.24960 |
| 261.22 | 148.55 | 75.72 | 70.859 | 20.20 | 9.1766 | 5.62 | 0.23952 |
| 257.14 | 148.02 | 74.66 | 69.965 | 19.87 | 8.7947 | 5.54 | 0.22983 |
| 253.02 | 147.74 | 73.63 | 69.067 | 19.61 | 8.4794 | 5.45 | 0.22093 |
| 248.91 | 147.34 | 72.58 | 68.161 | 19.33 | 8.1474 | 5.37 | 0.21260 |
| 244.82 | 146.52 | 71.55 | 67.253 | 19.02 | 7.7921 | 5.28 | 0.20444 |
| 240.71 | 145.80 | 70.52 | 66.326 | 18.63 | 7.3831 | 5.20 | 0.19678 |
| 236.60 | 144.76 | 69.46 | 65.342 | 18.40 | 7.1413 | 5.12 | 0.18957 |
| 232.49 | 143.72 | 68.45 | 64.351 | 18.05 | 6.7913 | 5.05 | 0.18253 |
| 228.38 | 142.94 | 67.37 | 63.336 | 17.83 | 6.5588 | 4.97 | 0.17529 |
| 224.26 | 141.92 | 66.36 | 62.325 | 17.50 | 6.2451 | 4.89 | 0.16922 |
| 298.44 | 150.31 | 65.33 | 61.283 | 17.26 | 6.0007 | 4.81 | 0.16271 |
| 294.01 | 150.46 | 64.29 | 60.232 | 16.98 | 5.7453 | 4.74 | 0.15676 |
| 289.93 | 149.89 | 63.28 | 59.191 | 16.71 | 5.5090 | 4.67 | 0.15113 |
| 285.82 | 149.43 | 62.21 | 58.128 | 16.46 | 5.2871 | 4.59 | 0.14569 |
| 281.73 | 149.17 | 61.19 | 57.077 | 15.19 | 5.0570 | 4.53 | 0.14069 |
| 277.62 | 149.45 | 50.14 | 56.013 | 15.93 | 4.8413 | 4.46 | 0.13668 |
| 213.32 | 149.59 | 59.11 | 54.951 | 15.09 | 4.0420 | 4.40 | 0.13270 |
| 269.43 | 149.21 | 58.00 | 03.880 59.707 | 15.44 | 4.4380 | 4.33 | 0.12729 |
| 200.04 | 148.90 | 56.01 | 51 601 | 14.06 | 4.2445 | 4.27 | 0.12332 |
| 257.14 | 147.86 | 54.98 | 50 565 | 14.50 14.73 | 3 8884 | 4.21 | 0.11501 |
| 253.02 | 147.68 | 53.03 | 49.409 | 14.70 | 3 7147 | 4.08 | 0.11167 |
| 248.92 | 147.15 | 52.89 | 48 237 | 14.45 | 3 5466 | 4.02 | 0.10681 |
| 244 82 | 146 41 | 51.87 | 47.086 | 14 04 | 3 3925 | 3.96 | 0 10417 |
| 240.71 | 145.63 | 50.82 | 45.966 | 13.82 | 3.2445 | 3.90 | 0.10116 |
| 236.61 | 144 68 | 49.78 | 44 771 | 13 60 | 3 1012 | 3.84 | $9.8110 \cdot 10^{-2}$ |
| 232.49 | 1/3 61 | 48.75 | 43 566 | 13 30 | 2 9653 | 378 | $9.5240.10^{-2}$ |
| 202.40 | 142.02 | 47.74 | 49.800 | 13.18 | 2.5005 | 3 73 | $0.2240 \cdot 10^{-2}$ |
| 220.00 | 142.92 | 46.70 | 42.547 | 12.13 | 2.0524 | 3.68 | $9.2290.10^{-2}$ |
| 224.29 | 141.09 | 40.70 | 41.101 | 12.97 | 2.7042 | 0.00 | 9.0240.10 |
| 220.16 | 140.75 | 45.00 | 39.889 | 12.77 | 2.0822 | 3.01 | $8.7210 \cdot 10$ |
| 216.06 | 139.89 | 45.66 | 39.880 | 12.57 | 2.4684 | 3.56 | $8.5010 \cdot 10^{-2}$ |
| 211.94 | 138.80 | 45.12 | 39.234 | 12.37 | 2.3554 | 3.51 | $8.3120 \cdot 10^{-2}$ |
| 207.84 | 137.72 | 44.60 | 38.616 | 12.18 | 2.2514 | 3.46 | $8.1080 \cdot 10^{-2}$ |
| 203.72 | 136.85 | 44.08 | 38.031 | 11.99 | 2.1480 | 3.41 | $7.9860 \cdot 10^{-2}$ |
| 199.59 | 135.65 | 43.57 | 37.429 | 11.80 | 2.0471 | 3.37 | $7.8210 \cdot 10^{-2}$ |
| 195.49 | 134.41 | 43.05 | 36.821 | 11.61 | 1.9534 | 3.32 | $7.6230 \cdot 10^{-2}$ |
| 191.37 | 132.98 | 42.53 | 36.209 | 11.43 | 1.8609 | 3.27 | $7.4610 \cdot 10^{-2}$ |
| 187.26 | 131.58 | 42.01 | 35.596 | 11.24 | 1.7761 | 3.23 | $7.3660 \cdot 10^{-2}$ |
| 183.14 | 130.38 | 41.50 | 34.980 | 11.07 | 1.6978 | 3.18 | $7.1800 \cdot 10^{-2}$ |
| 179.02 | 129.08 | 40.96 | 34.338 | 10.89 | 1.6220 | 3.13 | $7.0580 \cdot 10^{-2}$ |
| 174.90 | 127.64 | 40.34 | 33.623 | 10.72 | 1.5477 | 3.08 | $6.8430 \cdot 10^{-2}$ |
| 170.78 | 126.15 | 39.85 | 33.082 | 10.56 | 1.4775 | 3.04 | $6.7060 \cdot 10^{-2}$ |
| 166.67 | 124.67 | 39.32 | 32.475 | 10.39 | 1,4086 | 3.00 | $6.5610 \cdot 10^{-2}$ |
| 162.55 | 123 14 | 38 80 | 31.875 | 10.23 | 1.3448 | 2.95 | $6.4510 \cdot 10^{-2}$ |
| 158 43 | 121.57 | 38.28 | 31 284 | 10.07 | 1 2850 | 2.91 | $6.3420 \cdot 10^{-2}$ |
| 154 30 | 121.01 | 37.77 | 30.678 | 0.01 | 1.2000 | 2.01 | 6.2300.10 ⁻² |
| 150 10 | 110.01 | 01.11 97 07 | 20.070 | 9.91 0.76 | 1.44/0 | 4.00 0.04 | 0.2390.10 6 1410 10 ⁻² |
| 100.18 | 116.30 | 31.21 26 74 | au.10a | 9.70 | 1.1/1/ | ⊿.84 2.80 | 0.1410.10 |
| 140.05 | 110.73 | 30.74 | 29.492 | 9.61 | 1.1175 | 2.80 | $0.0330 \cdot 10^{-2}$ |
| 141.92 | 114.85 | 30.23 | 28.901 | 9.46 | 1.0101 | 2.76 | 5.9840·10 - 5.9840·10 -2 |
| 137.79 | 112.97 | 35.70 | 28.300 | 9.31 | 1.0164 | 2.73 | $5.8780 \cdot 10^{-2}$ |
| 133.66 | 110.94 | 35.19 | 27.709 | 9.16 | 0.97051 | 2.69 | $5.8210 \cdot 10^{-2}$ |
| 129.51 | 108.52 | 34.67 | 27.125 | 9.02 | 0.92699 | 2.65 | $5.7300 \cdot 10^{-2}$ |
| 125.39 | 106.47 | 34.16 | 26.554 | 8.88 | 0.88453 | 2.62 | $5.6670 \cdot 10^{-2}$ |

Table 5: Experimental heat capacity data for K_2NpO_4 .

| T | $C_{n m}^{o}$ | Т | $C_{n m}^{o}$ | T | $C_{n m}^{o}$ | T | C_{n}^{o} |
|--------|--|-------|--|------|--|------|--|
| (K) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ | (K) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ | (K) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ | (K) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ |
| 121.26 | 104.23 | 33.64 | 25.977 | 8.74 | 0.84464 | 2.58 | $5.5870 \cdot 10^{-2}$ |
| 117.14 | 101.86 | 33.12 | 25.399 | 8.61 | 0.80641 | 2.55 | $5.4840 \cdot 10^{-2}$ |
| 113.00 | 99.342 | 32.61 | 24.834 | 8.47 | 0.76952 | 2.52 | $5.4310 \cdot 10^{-2}$ |
| 108.85 | 96.705 | 32.10 | 24.250 | 8.34 | 0.73372 | 2.49 | $5.3670 \cdot 10^{-2}$ |
| 104.73 | 93.925 | 31.58 | 23.682 | 8.21 | 0.70041 | 2.46 | $5.2780 \cdot 10^{-2}$ |
| 100.59 | 90.936 | 31.07 | 23.119 | 8.08 | 0.66801 | 2.43 | $5.2170 \cdot 10^{-2}$ |
| 96.44 | 87.774 | 30.55 | 22.574 | 7.96 | 0.63753 | 2.40 | $5.1490 \cdot 10^{-2}$ |
| 96.49 | 87.826 | 30.05 | 22.049 | 7.83 | 0.60685 | 2.37 | $5.0650 \cdot 10^{-2}$ |
| 95.35 | 86.884 | 29.56 | 21.568 | 7.71 | 0.57981 | 2.34 | $5.0040 \cdot 10^{-2}$ |
| 94.31 | 86.108 | 29.03 | 21.068 | 7.59 | 0.55302 | 2.31 | $4.9240 \cdot 10^{-2}$ |
| 93.28 | 85.263 | 28.51 | 20.624 | 7.48 | 0.52777 | 2.28 | $4.8980 \cdot 10^{-2}$ |
| 92.24 | 84.467 | 28.00 | 20.227 | 7.36 | 0.50407 | 2.26 | $4.8450 \cdot 10^{-2}$ |
| 91.22 | 83.658 | 27.48 | 19.908 | 7.25 | 0.48099 | 2.23 | $4.7590 \cdot 10^{-2}$ |
| 90.19 | 82.867 | 26.95 | 19.755 | 7.13 | 0.45942 | 2.21 | $4.7150 \cdot 10^{-2}$ |
| 89.16 | 82.003 | 26.47 | 19.827 | 6.93 | 0.42253 | 2.18 | $4.6610 \cdot 10^{-2}$ |
| 88.12 | 81.115 | 25.96 | 19.738 | 6.78 | 0.39766 | 2.16 | $4.6260 \cdot 10^{-2}$ |
| 87.08 | 80.204 | 25.46 | 18.459 | 6.68 | 0.38007 | 2.13 | $4.5250 \cdot 10^{-2}$ |
| 86.05 | 79.395 | 24.95 | 17.054 | 6.58 | 0.36403 | | |

Experimental heat capacity data for K_2NpO_4 (continued).

| T | C° | T | C^{0} | T | C° | T | C° |
|--------|-----------------------------------|----------------|-----------------------------------|----------------|--|--------------|-----------------------------------|
| (K) | $(J \cdot K^{-1} \cdot mol^{-1})$ | (K) | $(J \cdot K^{-1} \cdot mol^{-1})$ | (K) | $(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})$ | (K) | $(J \cdot K^{-1} \cdot mol^{-1})$ |
| 312.40 | 161.60 | 87.12 | <u>82.810</u> | 27.38 | 15 298 | 7 48 | 0.39842 |
| 312.39 | 160.58 | 87.12 | 82.832 | 26.87 | 14.665 | 7.48 | 0.39873 |
| 312.43 | 160.24 | 83.06 | 79.366 | 26.88 | 14.708 | 7.49 | 0.39950 |
| 308.36 | 159.08 | 83.08 | 79.371 | 26.88 | 14.710 | 7.31 | 0.36697 |
| 308.60 | 159.45 | 83.07 | 79.384 | 26.36 | 14.113 | 7.31 | 0.36579 |
| 308.62 | 159.18 | 79.01 | 75.676 | 26.37 | 14.124 | 7.31 | 0.36601 |
| 304.47 | 158.20 | 79.03 | 75.691 | 26.36 | 14.118 | 7.13 | 0.33632 |
| 304.70 | 158.39 | 79.03 | 75.666 | 25.85 | 13.545 | 7.14 | 0.33672 |
| 304.69 | 158.12 | 74.96 | 71.826 | 25.86 | 13.552 | 7.14 | 0.33674 |
| 300.55 | 157.42 | 74.98 | 71.838 | 25.86 | 13.538 | 6.99 | 0.31321 |
| 300.75 | 157.55 | 74.97 | 71.820 | 25.35 | 12.967 | 6.99 | 0.31255 |
| 300.73 | 157.45 | 70.92 | 67.795 | 25.36 | 12.993 | 6.99 | 0.31434 |
| 296.58 | 156.80 | 70.93 | 67.829 | 25.35 | 12.988 | 6.81 | 0.28615 |
| 296.75 | 157.07 | 70.93 | 67.795 | 24.84 | 12.425 | 6.82 | 0.28738 |
| 296.76 | 156.87 | 66.87 | 63.596 | 24.85 | 12.432 | 6.82 | 0.28696 |
| 292.59 | 156.14 | 66.89 | 63.611 | 24.85 | 12.431 | 6.65 | 0.26296 |
| 292.77 | 156.35 | 66.88 | 63.570 | 24.33 | 11.897 | 6.66 | 0.26242 |
| 292.78 | 156.33 | 62.82 | 59.113 | 24.34 | 11.883 | 6.66 | 0.26271 |
| 288.60 | 155.09 | 62.84 | 59.113 | 24.34 | 11.875 | 6.50 | 0.24180 |
| 288.78 | 155.43 | 62.84 | 59.100 | 23.83 | 11.364 | 6.50 | 0.24290 |
| 288.76 | 155.30 | 58.78 | 54.552 | 23.84 | 11.333 | 6.50 C.24 | 0.24231 |
| 284.60 | 154.49 | 58.79 | 54.568 | 23.83 | 11.327 | 6.34 0.95 | 0.22326 |
| 284.76 | 154.64 | 58.79 | 54.563 | 23.32 | 10.786 | 6.35 C.95 | 0.22277 |
| 284.75 | 154.00 | 04.74 E4.75 | 49.801 | 23.33 | 10.798 | 0.30 | 0.22412 |
| 280.39 | 154.01 | 54.75 | 49.810 | ⊿ə.əə 99.91 | 10.769 | 6.20 | 0.20715 |
| 280.75 | 154.55 | 50.60 | 49.795 | 22.01 | 10.294 | 6.20 | 0.20732 |
| 260.74 | 159.79 | 50.09 | 44.917 | 22.62 | 10.275 | 6.05 | 0.120394 |
| 276.38 | 153.70 | 50.70 | 44.927 | 22.62 | 0.7523 | 6.05 | 0.18998 |
| 276.73 | 153.81 | 50.03 | 44.910 | 22.31 | 9.7381 | 6.06 | 0.19010 |
| 279.57 | 153.51 | 50.69 | 44.900 | 22.01 | 9.7462 | 5.01 | 0.17522 |
| 272.73 | 153.16 | 50.69 | 44.898 | 21.80 | 9.2319 | 5.91 | 0.17396 |
| 272.71 | 153 29 | 50.00 | 44 249 | 21.80 | 9 2338 | 5.91 | 0 17499 |
| 268.56 | 152.73 | 50.19 | 44.281 | 21.80 | 9.2329 | 5.77 | 0.16011 |
| 268.70 | 152.83 | 50.19 | 44.279 | 21.30 | 8.7270 | 5.77 | 0.16012 |
| 268.70 | 152.83 | 49.66 | 43.617 | 21.30 | 8.7410 | 5.78 | 0.16111 |
| 264.55 | 152.10 | 49.68 | 43.655 | 21.30 | 8.7381 | 5.64 | 0.14760 |
| 264.67 | 152.31 | 49.68 | 43.657 | 20.79 | 8.2552 | 5.64 | 0.14831 |
| 264.68 | 152.29 | 49.15 | 42.987 | 20.79 | 8.2590 | 5.64 | 0.14809 |
| 260.53 | 151.17 | 49.18 | 43.031 | 20.79 | 8.2572 | 5.50 | 0.13636 |
| 260.65 | 151.44 | 49.17 | 43.034 | 20.28 | 7.7823 | 5.51 | 0.13711 |
| 260.65 | 151.42 | 48.65 | 42.348 | 20.29 | 7.7952 | 5.51 | 0.13768 |
| 256.51 | 150.55 | 48.67 | 42.386 | 20.28 | 7.7825 | 5.37 | 0.12648 |
| 256.63 | 150.70 | 48.67 | 42.395 | 20.27 | 7.7659 | 5.38 | 0.12664 |
| 256.64 | 150.67 | 48.14 | 41.723 | 20.28 | 7.7866 | 5.38 | 0.12708 |
| 252.49 | 150.01 | 48.17 | 41.768 | 20.28 | 7.7918 | 5.25 | 0.11747 |
| 252.62 | 150.18 | 48.16 | 41.762 | 19.81 | 7.3540 | 5.25 | 0.11869 |
| 252.62 | 150.10 | 47.63 | 41.077 | 19.82 | 7.3927 | 5.25 | 0.11884 |
| 248.48 | 149.37 | 47.66 | 41.126 | 19.80 | 7.3481 | 5.13 | 0.10952 |
| 248.61 | 149.51 | 47.00 | 41.132 | 19.34 | 6.9356 | 5.13 | 0.10936 |
| 248.59 | 149.50 | 47.15 | 40.445 | 19.30 | 0.9582 | 0.13 E 01 | 0.11049 |
| 244.40 | 148.52 | 47.10 | 40.460 | 19.54 | 0.9330 | 5.01 | 0.10157 |
| 244.57 | 148.71 | 47.10 | 40.493 | 18.88 | 0.0373 | 5.01 | $9.9880 \cdot 10$ |
| 244.57 | 148.83 | 40.62 | 39.810 | 18.89 | 0.5427 | 0.01 | 9.9880.10 - |
| 240.45 | 147.78 | 46.64 | 39.857 | 18.89 | 6.5436 | 4.89 | $9.2890 \cdot 10^{-2}$ |
| 240.54 | 147.84 | 46.64 | 39.840 | 18.45 | 6.1579 | 4.89 | $9.2690 \cdot 10^{-2}$ |
| 240.54 | 147.89 | 46.11 | 39.162 | 18.45 | 6.1755 | 4.89 | $9.2930 \cdot 10^{-2}$ |
| 236.41 | 146.85 | 46.14 | 39.196 | 18.44 | 6.1673 | 4.77 | $8.5980 \cdot 10^{-2}$ |
| 236.51 | 147.02 | 46.14 | 39.195 | 18.00 | 5.8038 | 4.77 | $8.6130 \cdot 10^{-2}$ |
| 236.52 | 146.91 | 45.61 | 38.528 | 18.02 | 5.8147 | 4.77 | $8.6140 \cdot 10^{-2}$ |
| 232.38 | 145.84 | 45.63 | 38.551 | 18.02 | 5.8141 | 4.66 | $7.9830 \cdot 10^{-2}$ |
| 232.49 | 145.96 | 45.63 | 38.555 | 17.59 | 5.4622 | 4.66 | $7.9230 \cdot 10^{-2}$ |
| 232.48 | 146.02 | 45.10 | 37.870 | 17.60 | 5.4785 | 4.66 | $7.9820 \cdot 10^{-2}$ |

Table 6: Experimental heat capacity data for K_2UO_4 .

| Т | C° | Т | C° | Т | C° | T | C° |
|------------------|--|----------------|--|----------------|--|---------------|--|
| (K) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ | (K) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ | (K) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ | (K) | $(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})$ |
| 228.37 | 145.08 | 45.12 | 37.912 | 17.59 | 5.4739 | 4.55 | $\frac{(0.11 - 1101)}{7.3160 \cdot 10^{-2}}$ |
| 228.46 | 145.10 | 45.12 | 37.900 | 17.18 | 5.1504 | 4.55 | $7.5280 \cdot 10^{-2}$ |
| 228.46 | 145.05 | 44.59 | 37.224 | 17.19 | 5.1550 | 4.55 | $7.4780 \cdot 10^{-2}$ |
| 224.34 | 144.24 | 44.62 | 37.256 | 17.18 | 5.1531 | 4.43 | $6.9070 \cdot 10^{-2}$ |
| 224.43 | 144.37 | 44.62 | 37.253 | 16.78 | 4.8408 | 4.44 | $6.8680 \cdot 10^{-2}$ |
| 224.45 | 144.34 | 44.09 | 36.556 | 16.78 | 4.8519 | 4.44 | $6.8210 \cdot 10^{-2}$ |
| 220.32 | 143.30 | 44.11 | 36.599 | 16.78 | 4.8467 | 4.33 | $6.4690 \cdot 10^{-2}$ |
| 220.41 | 143.41 | 44.11 | 36.593 | 16.38 | 4.5597 | 4.34 | $6.3390 \cdot 10^{-2}$ |
| 220.41 | 143.31 | 43.58 | 35.903 | 16.39 | 4.5603 | 4.33 | $6.5490 \cdot 10^{-2}$ |
| 216.30 | 142.33 | 43.60 | 35.944 | 16.38 | 4.5552 | 4.23 | $5.9750 \cdot 10^{-2}$ |
| 216.38 | 142.31 | 43.60 | 35.937 | 15.99 | 4.2725 | 4.24 | $6.0840 \cdot 10^{-2}$ |
| 216.38 | 142.39 | 43.07 | 35.257 | 16.01 | 4.2816 | 4.23 | $5.9510 \cdot 10^{-2}$ |
| 212.25 | 141.24 | 43.10 | 35.298 | 16.00 | 4.2775 | 4.13 | $5.5180 \cdot 10^{-2}$ |
| 212.35 | 141.40 | 43.09 | 35.283 | 15.62 | 4.0126 | 4.13 | $5.5460 \cdot 10^{-2}$ |
| 212.35 | 141.41 | 42.57 | 34.597 | 15.63 | 4.0163 | 4.13 | $5.5940 \cdot 10^{-2}$ |
| 208.24 | 140.15 | 42.59 | 34.632 | 15.62 | 4.0155 | 4.04 | $5.2470 \cdot 10^{-2}$ |
| 208.31 | 140.22 | 42.59 | 34.626 | 15.25 | 3.7646 | 4.04 | $5.1320 \cdot 10^{-2}$ |
| 208.31 | 140.24 | 42.06 | 33.939 | 15.26 | 3.7745 | 4.04 | $5.1380 \cdot 10^{-2}$ |
| 204.21 | 139.07 | 42.08 | 33.967 | 15.26 | 3.7716 | 3.94 | $4.7470 \cdot 10^{-2}$ |
| 204.28 | 139.22 | 42.08 | 33.973 | 14.89 | 3.5300 | 3.94 | $4.7740 \cdot 10^{-2}$ |
| 204.28 | 139.20 | 41.55 | 33.272 | 14.91 | 3.5349 | 3.94 | $4.7650 \cdot 10^{-2}$ |
| 200.18 | 138.00 | 41.57 | 33.311 | 14.90 | 3.3374 | 3.85 2.05 | $4.4080 \cdot 10^{-2}$ |
| 200.25 | 138.00 | 41.57 | 33.3U1 29.610 | 14.54 14 55 | 3.3U81 9.9117 | 3.85 2 0 E | $4.4000 \cdot 10^{-2}$ |
| 200.26 | 138.04 | 41.05 | 32.019 | 14.55 | 3.3117 2.2141 | 3.80 | $4.4200 \cdot 10$ $4.1200 \cdot 10^{-2}$ |
| 190.14 | 136.02 | 41.07 | 32.000 | 14.55 | 3.0047 | 3.70 | $4.1200 \cdot 10$ $4.0050 \cdot 10^{-2}$ |
| 106.22 | 136.94 | 40.54 | 31.057 | 14.20 | 3 1007 | 3.76 | $4.0930\cdot10^{-2}$ |
| 190.22 | 135.68 | 40.54 | 31.988 | 14.21 | 3.1007 | 3.67 | $3.8110.10^{-2}$ |
| 192.11 192.18 | 135.77 | 40.50 40.56 | 31 994 | 13.86 | 2 8953 | 3.67 | $3.8120 \cdot 10^{-2}$ |
| 192.18 | 135.71 | 40.03 | 31 302 | 13.88 | 2.0000 | 3 67 | $3.7950 \cdot 10^{-2}$ |
| 188.08 | 134 47 | 40.05 | 31 333 | 13.88 | 2 9038 | 3 58 | $35360 \cdot 10^{-2}$ |
| 188.15 | 134.52 | 40.05 | 31.327 | 13.54 | 2.7124 | 3.58 | $3.5480 \cdot 10^{-2}$ |
| 188.15 | 134.53 | 39.53 | 30.648 | 13.55 | 2.7109 | 3.59 | $3.4990 \cdot 10^{-2}$ |
| 184.05 | 133.29 | 39.55 | 30.675 | 13.55 | 2.7155 | 3.50 | $3.2930 \cdot 10^{-2}$ |
| 184.12 | 133.26 | 39.54 | 30.670 | 13.22 | 2.5316 | 3.50 | $3.3200 \cdot 10^{-2}$ |
| 184.12 | 133.26 | 39.02 | 29.987 | 13.23 | 2.5347 | 3.50 | $3.3020 \cdot 10^{-2}$ |
| 180.04 | 132.01 | 39.04 | 30.021 | 13.23 | 2.5353 | 3.42 | $3.0580 \cdot 10^{-2}$ |
| 180.08 | 132.13 | 39.04 | 30.024 | 12.91 | 2.3572 | 3.42 | $3.0950 \cdot 10^{-2}$ |
| 180.09 | 132.04 | 38.51 | 29.340 | 12.92 | 2.3644 | 3.42 | $3.1160 \cdot 10^{-2}$ |
| 176.01 | 130.65 | 38.53 | 29.374 | 12.93 | 2.3676 | 3.34 | $2.8860 \cdot 10^{-2}$ |
| 176.07 | 130.70 | 38.53 | 29.372 | 12.61 | 2.2034 | 3.34 | $2.8800 \cdot 10^{-2}$ |
| 176.06 | 130.71 | 38.01 | 28.672 | 12.62 | 2.2060 | 3.34 | $2.8840 \cdot 10^{-2}$ |
| 171.98 | 129.24 | 38.03 | 28.718 | 12.62 | 2.2045 | 3.26 | $2.6860 \cdot 10^{-2}$ |
| 172.03 | 129.28 | 38.02 | 28.704 | 12.32 | 2.0549 | 3.26 | $2.6890 \cdot 10^{-2}$ |
| 172.03 | 129.36 | 37.50 | 28.029 | 12.33 | 2.0561 | 3.26 | $2.6860 \cdot 10^{-2}$ |
| 167.95 | 127.94 | 37.52 | 28.062 | 12.33 | 2.0611 | 3.18 | $2.4880 \cdot 10^{-2}$ |
| 167.99 | 127.95 | 37.52 | 28.053 | 12.03 | 1.9146 | 3.18 | $2.4850 \cdot 10^{-2}$ |
| 167.98 | 127.97 | 36.99 | 27.374 | 12.03 | 1.9176 | 3.19 | $2.5250 \cdot 10^{-2}$ |
| 163.91 | 126.51 | 37.01 | 27.396 | 12.03 | 1.9171 | 3.11 | $2.3250 \cdot 10^{-2}$ |
| 163.95 | 120.51 | 37.UI 26.40 | 27.398 | 11.74 | 1.7803 | 3.11 2.11 | $2.3400 \cdot 10^{-1}$ |
| 153.95 | 126.51 | 36.49 | 26.708 | 11.75 | 1.7835 | 3.11 | $2.3410 \cdot 10^{-2}$ |
| 150.01 | 120.01 | 30.51 26 51 | 20.730 | 11.76 | 1.(871 | 3.04 2.04 | $2.1900 \cdot 10^{-2}$ |
| 159.91 | 120.04 | 35.08 | 20.120 26.043 | 11.47 | 1.0002 | 3.04 | 2.1950.10 2.2000.10 ⁻² |
| 155.91 | 124.90 | 36.00 | 20.043 | 11.40 | 1.6570 | 0.04 0.07 | $2.2000.10^{-2}$ |
| 155.86 | 123.30 | 36.00 | 26.063 | 11.40 | 1.5409 | 2.91 2.07 | $2.0570.10^{-2}$ |
| 155.86 | 123.40 | 35.00 35.47 | 25 373 | 11.20 | 1 5428 | 2.97 | $2.0320 \cdot 10^{-2}$ |
| 151.80 | 121 75 | 35 49 | 25.428 | 11.21 | 1.5440 | 2.90 | $1.9310 \cdot 10^{-2}$ |
| 151.82 | 121.69 | 35.49 | 25,405 | 10.94 | 1,4302 | 2.90 | $1.9280 \cdot 10^{-2}$ |
| 151.82 | 121.73 | 34.97 | 24.741 | 10.95 | 1.4306 | 2.90 | $1.9470 \cdot 10^{-2}$ |
| 147.77 | 120.09 | 34.99 | 24.771 | 10.95 | 1.4322 | 2.83 | $1.5950 \cdot 10^{-2}$ |
| 147.79 | 120.08 | 34.98 | 24.253 | 10.68 | 1.3259 | 2.84 | $1.6010 \cdot 10^{-2}$ |
| 147.78 | 120.10 | 34.46 | 24.083 | 10.69 | 1.3300 | 2.84 | $1.6110 \cdot 10^{-2}$ |
| | | | | | | | |

Experimental heat capacity data for K_2UO_4 (continued).

| <i>T</i> | C° | Т | C° | Т | C° | T | C° |
|------------------|--|-------|--|-------|--|------|--|
| (\overline{K}) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ | (K) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ | (K) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ | (K) | $(\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$ |
| 143.72 | 118.36 | 34.48 | 24.123 | 10.69 | 1.3315 | 2.77 | $1.5000 \cdot 10^{-2}$ |
| 143.74 | 118.34 | 34.48 | 24.103 | 10.44 | 1.2310 | 2.77 | $1.4920 \cdot 10^{-2}$ |
| 143.74 | 118.34 | 33.95 | 23.439 | 10.44 | 1.2313 | 2.77 | $1.4920 \cdot 10^{-2}$ |
| 139.68 | 116.38 | 33.98 | 23.462 | 10.44 | 1.2311 | 2.70 | $1.4020 \cdot 10^{-2}$ |
| 139.70 | 116.40 | 33.97 | 23.458 | 10.19 | 1.1384 | 2.70 | $1.3910 \cdot 10^{-2}$ |
| 139.70 | 116.34 | 33.45 | 22.780 | 10.20 | 1.1408 | 2.70 | $1.3920 \cdot 10^{-2}$ |
| 135.65 | 114.34 | 33.47 | 22.821 | 10.20 | 1.1419 | 2.64 | $1.3010 \cdot 10^{-2}$ |
| 135.66 | 114.35 | 33.47 | 22.802 | 9.96 | 1.0551 | 2.64 | $1.2920 \cdot 10^{-2}$ |
| 135.66 | 114.31 | 32.95 | 22.152 | 9.96 | 1.0561 | 2.64 | $1.2950 \cdot 10^{-2}$ |
| 131.61 | 112.28 | 32.96 | 22.160 | 9.96 | 1.0556 | 2.57 | $1.2100 \cdot 10^{-2}$ |
| 131.62 | 112.26 | 32.96 | 22.171 | 9.72 | 0.97401 | 2.57 | $1.2060 \cdot 10^{-2}$ |
| 131.62 | 112.24 | 32.44 | 21.504 | 9.73 | 0.97647 | 2.57 | $1.1990 \cdot 10^{-2}$ |
| 127.57 | 110.10 | 32.46 | 21.535 | 9.73 | 0.97672 | 2.52 | $1.1270 \cdot 10^{-2}$ |
| 127.57 | 110.10 | 32.45 | 21.528 | 9.49 | 0.90085 | 2.52 | $1.1280 \cdot 10^{-2}$ |
| 127.57 | 110.07 | 31.94 | 20.870 | 9.50 | 0.90027 | 2.52 | $1.1220 \cdot 10^{-2}$ |
| 123.53 | 107.89 | 31.95 | 20.889 | 9.50 | 0.90100 | 2.46 | $1.0530 \cdot 10^{-2}$ |
| 123.54 | 107.84 | 31.95 | 20.889 | 9.26 | 0.83045 | 2.46 | $1.0520 \cdot 10^{-2}$ |
| 123.54 | 107.87 | 31.43 | 20.234 | 9.28 | 0.83169 | 2.45 | $1.0470 \cdot 10^{-2}$ |
| 119.50 | 105.45 | 31.44 | 20.255 | 9.28 | 0.83279 | 2.40 | $9.8700 \cdot 10^{-3}$ |
| 119.49 | 105.44 | 31.44 | 20.243 | 9.04 | 0.76799 | 2.40 | $9.7700 \cdot 10^{-3}$ |
| 119.49 | 105.39 | 30.92 | 19.595 | 9.05 | 0.76806 | 2.40 | $9.8000 \cdot 10^{-3}$ |
| 115.45 | 103.00 | 30.94 | 19.608 | 9.05 | 0.76923 | 2.34 | $9.2100 \cdot 10^{-3}$ |
| 115.45 | 102.98 | 30.94 | 19.614 | 8.83 | 0.70691 | 2.34 | $9.1500 \cdot 10^{-3}$ |
| 115.45 | 103.04 | 30.42 | 18.957 | 8.84 | 0.70762 | 2.34 | $9.1500 \cdot 10^{-3}$ |
| 111.41 | 100.48 | 30.43 | 18.977 | 8.84 | 0.70842 | 2.29 | $8.5700 \cdot 10^{-3}$ |
| 111.39 | 100.46 | 30.43 | 18.980 | 8.63 | 0.65315 | 2.29 | $8.5500 \cdot 10^{-3}$ |
| 111.40 | 100.52 | 29.91 | 18.341 | 8.63 | 0.65340 | 2.29 | $8.5400 \cdot 10^{-3}$ |
| 107.35 | 97.856 | 29.92 | 18.351 | 8.63 | 0.65412 | 2.24 | $7.9200 \cdot 10^{-3}$ |
| 107.35 | 97.839 | 29.92 | 18.341 | 8.42 | 0.60171 | 2.24 | $7.9300 \cdot 10^{-3}$ |
| 107.34 | 97.805 | 29.39 | 17.716 | 8.43 | 0.60040 | 2.23 | $7.9100 \cdot 10^{-3}$ |
| 103.30 | 95.053 | 29.42 | 17.736 | 8.43 | 0.60089 | 2.18 | $7.4100 \cdot 10^{-3}$ |
| 103.30 | 95.047 | 29.41 | 17.722 | 8.23 | 0.55410 | 2.18 | $7.3900 \cdot 10^{-3}$ |
| 103.30 | 95.013 | 28.89 | 17.095 | 8.23 | 0.55396 | 2.18 | $7.3700 \cdot 10^{-3}$ |
| 99.25 | 92.193 | 28.91 | 17.120 | 8.23 | 0.55480 | 2.14 | $6.8700 \cdot 10^{-3}$ |
| 99.25 | 92.172 | 28.90 | 17.110 | 8.03 | 0.51232 | 2.14 | $6.8600 \cdot 10^{-3}$ |
| 99.25 | 92.192 | 28.39 | 16.504 | 8.04 | 0.51177 | 2.14 | $6.8500 \cdot 10^{-3}$ |
| 95.21 | 89.272 | 28.39 | 16.497 | 8.04 | 0.51178 | 2.09 | $6.3900 \cdot 10^{-3}$ |
| 95.20 | 89.273 | 28.40 | 16.507 | 7.84 | 0.47083 | 2.09 | $6.3700 \cdot 10^{-3}$ |
| 95.21 | 89.216 | 27.89 | 15.901 | 7.85 | 0.47006 | 2.09 | $6.3500 \cdot 10^{-3}$ |
| 91.16 | 86.179 | 27.89 | 15.903 | 7.85 | 0.47040 | 2.03 | $5.9000 \cdot 10^{-3}$ |
| 91.15 | 86.104 | 27.89 | 15.916 | 7.66 | 0.43254 | 2.03 | $5.8700 \cdot 10^{-3}$ |
| 91.16 | 86.112 | 27.38 | 15.285 | 7.67 | 0.43328 | 2.04 | $5.9200 \cdot 10^{-3}$ |
| 87.11 | 82.901 | 27.38 | 15.304 | 7.67 | 0.43355 | | |

Experimental heat capacity data for $\mathrm{K}_{2}\mathrm{UO}_{4}$ (continued).