

Temperature variation of the structural parameters in actinide tetrafluorides

S. Kern, J. Hayward, S. Roberts, J. W. Richardson Jr., F. J. Rotella, L. Soderholm, B. Cort, M. Tinkle, M. West, D. Hoisington, and G. H. Lander

Citation: *The Journal of Chemical Physics* **101**, 9333 (1994); doi: 10.1063/1.467963

View online: <http://dx.doi.org/10.1063/1.467963>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/101/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Evolution of the electronic structure of cyclic polythiophene upon bipolaron doping](#)

J. Chem. Phys. **105**, 11075 (1996); 10.1063/1.472908

[Conductive Cu\(2,5dimethyldicyanoquinonedimine\)₂ radical ion salts: Systems with none, one, or two phase transitions](#)

J. Chem. Phys. **105**, 6538 (1996); 10.1063/1.472496

[Role of collective modes in vibrational polarizabilities and hyperpolarizabilities of polyacetylene and other quasilinear polymers](#)

J. Chem. Phys. **104**, 4125 (1996); 10.1063/1.471540

[The reciprocal lattice as the Fourier transform of the direct lattice](#)

Am. J. Phys. **64**, 333 (1996); 10.1119/1.18243

[On finitesize effects in computer simulations using the Ewald potential](#)

J. Chem. Phys. **103**, 6133 (1995); 10.1063/1.470721



Temperature variation of the structural parameters in actinide tetrafluorides

S. Kern

Department of Physics, Colorado State University, Fort Collins, Colorado 80523 and Intense Pulsed Neutron Division, Argonne National Laboratory, Argonne, Illinois 60439

J. Hayward and S. Roberts

Department of Physics, Colorado State University, Fort Collins, Colorado 80523

J. W. Richardson, Jr. and F. J. Rotella

Intense Pulsed Neutron Division, Argonne National Laboratory, Argonne, Illinois 60439

L. Soderholm

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

B. Cort, M. Tinkle,^{a)} M. West, and D. Hoisington

Nuclear Materials Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

G. H. Lander

European Commission, JRC, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany

(Received 29 April 1994; accepted 23 August 1994)

We have used neutron diffraction on polycrystalline samples of AnF_4 ($An=Th, U, \text{ and } Np$) to examine the structures. All are isostructural with monoclinic space group $C2/c$. The structure of UF_4 has been examined in some detail as a function of temperature. The volume of the unit cell has a minimum not at lowest temperature (15 K) examined, but rather at ~ 350 K. ThF_4 also has a larger volume at low rather than room temperature; suggesting that this effect is caused by structural rather than electronic (as ThF_4 has no $5f$ electrons) interactions. An examination of the coordination around the two independent An sites in UF_4 shows that the fluorine configuration changes appreciably around $An2$ as a function of temperature. At low temperatures the distorted cubic antiprism structure is considerably more "puckered" than at higher temperatures. This puckering requires more volume for the molecule, thus causing the volume to *expand* as the temperature is lowered. The temperature factors and the interatomic distances vary smoothly with temperature and show no unusual behavior. © 1994 American Institute of Physics.

I. INTRODUCTION

The structure of the actinide tetrafluorides at room temperature was previously studied by x-ray diffraction using powder¹ and single-crystal² material. The structure is monoclinic with space group $C2/c$ and the unit cell contains 12 U atoms, four U1 sites with C_2 symmetry, and eight U2 sites with C_s symmetry. Motivated by recent interest in the spectroscopic properties³ of these materials, we undertook a diffraction study to examine the structural parameters at low temperature (15 K), which corresponds to the temperature of our neutron inelastic scattering experiments.⁴ To our surprise, the volume of the unit cell of UF_4 *expands* on cooling from 300 to 15 K. To investigate this unusual behavior a more complete series of diffraction experiments and their analyses were undertaken and are reported in this paper. Since UF_4 contains unpaired $5f$ electrons, we undertook a brief study of the isostructural ThF_4 , which has no unpaired electrons, to determine whether the expansion was related to electronic effects. Similar behavior for both ThF_4 and UF_4 suggests that the behavior arises from lattice rather than elec-

tronic effects. We show that a changing configuration of the fluorine atoms, primarily around one of the actinide sites, forces the volume to expand on cooling, even though the thermal vibrations and interatomic distances vary smoothly on warming from the lowest temperatures.

II. EXPERIMENTS AND RESULTS

Both samples were prepared at Los Alamos National Laboratory. UF_4 was prepared by reducing UF_6 in a hydrogen atmosphere. The UF_4 sample was of excellent quality and was the one that was most thoroughly investigated. ThF_4 was prepared by fluorination of the dioxide. A further annealing was performed at Argonne, but the sample crystallinity was not as good as that of the UF_4 sample. A description of the preparation of the NpF_4 sample is given in the following paper.⁴ In this study a single run at 300 K was performed on NpF_4 to check the structure and ensure that secondary phases were not present.

The experiments were performed on the general purpose powder diffractometer (GPPD) at the intense pulsed neutron source at Argonne National Laboratory. The GPPD is a high-

^{a)}Deceased.

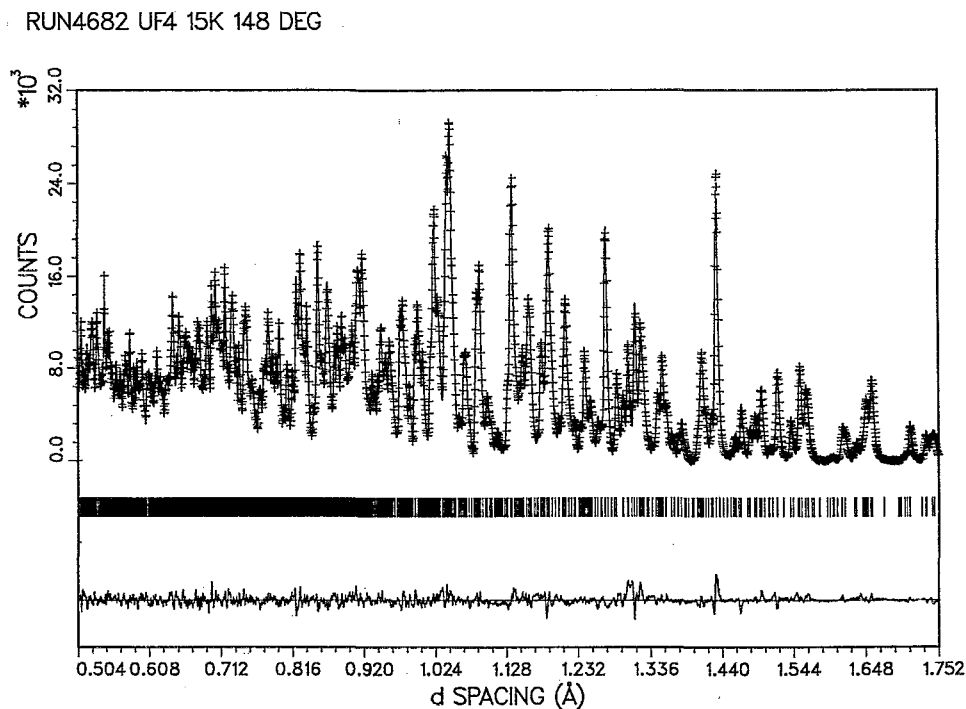


FIG. 1. Observed (points) and calculated (solid lines) diffraction patterns for UF_4 taken at 15 K. The vertical bars indicate discrete d spaces, and the pattern below is the difference between the observed and calculated patterns.

resolution instrument with detectors at various scattering angles; for the highest resolution of $\Delta d/d \sim 0.25\%$ we used the highest-angle bank of detectors centered on 148° from the incident beam. The polycrystalline sample of UF_4 (22 g), contained in vanadium, was run at temperatures from 15 to 625 K. For temperatures between 15 and 300 K a displex refrigerator was used; for higher temperatures a special furnace with a heating element made of vanadium was used. Because of slight positioning differences of the samples in the ancillary devices, the room temperature lattice parameters measured in the two different experiments differed by a scale factor of 1.000 284. All the lattice parameters measured in the furnace have therefore been renormalized by this amount. Such positioning errors do not affect the atomic or

thermal parameters. The ThF_4 sample was run only at 15 and 300 K.

Data analysis was performed on the total diffraction profile (the Rietveld method) with a suite of programs available at IPNS. The exceptional quality of the UF_4 sample, and the fit to the experimental data, can be judged from Fig. 1. Normally, with a large unit cell and the Rietveld programs about 4000 different reflections down to a d space of $\sim 0.4 \text{ \AA}$ are used, and then the intrinsic line broadening makes the refinement of further data meaningless. In this case the sharp lines from UF_4 allowed the extension of the method to a d space of 0.35 \AA , and included 10 000 reflections in the least-squares analysis.

The results for the cell parameters are given in Table I

TABLE I. Cell parameters for UF_4 as a function of temperature. The values in brackets are from Ref. 2. Standard deviations vary between 1 and 2 in the least-significant digit.

T (K)	15	50	100	200	300	420	523	625
a (\AA)	12.8051	12.8038	12.8001	12.7959	12.7941 [12.73]	12.7939	12.7964	12.7994
b (\AA)	10.7865	10.7849	10.7841	10.7861	10.7901 [10.75]	10.7955	10.7999	10.8040
c (\AA)	8.3758	8.3747	8.3717	8.3690	8.3687 [8.43]	8.3697	8.3715	8.3738
β (deg)	126.19	126.19	126.19	126.21	126.25 [126.3]	126.29	126.30	126.31
Vol. (\AA^3)	933.66	933.30	932.66	931.93	931.74 [929]	931.82	932.40	933.14

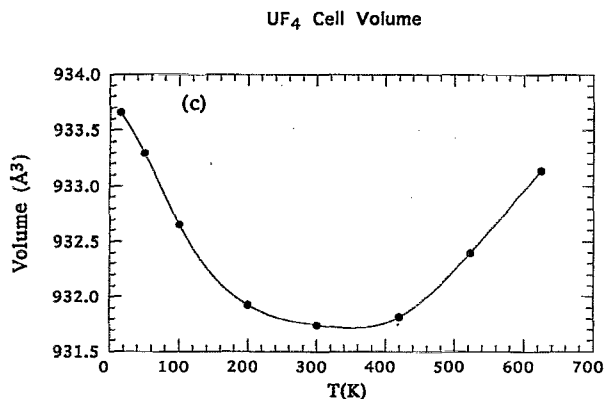


FIG. 2. The volume of the unit cell of UF_4 as a function of temperature. The lines are spline fits through the data points.

and the volume is plotted as a function of temperature in Fig. 2. The most striking aspect of this figure is that the volume *expands* on cooling from 300 to 15 K, with a minimum at ~ 350 K, and then expands in a more conventional way above this temperature. The same behavior is shown by both the *a* and *c* axes, whereas the *b* axis has its minimum near 100 K (see Table I). This unusual behavior of some of the lattice parameters and the volume is not accompanied by an anomalous behavior in the interatomic distances in the crystal; all of these change uniformly with temperature throughout the temperature range examined. Related to the interatomic distances is the volume of the thermal ellipsoid of each atom. In Fig. 3 we show the variation with temperature of the equivalent isotropic *B* parameters, as derived from the anisotropic thermal parameters given by the least-squares refinements.

The ThF_4 lattice parameters show the same effect, i.e., the volume is larger at 15 K than at 300 K, and to try to understand this effect we concentrate on the better data from the UF_4 refinements. Values for the parameters for ThF_4 and NpF_4 at selected temperatures are given in Table II.

The atomic parameters of UF_4 at 300 K are shown in Table III. They are in good agreement with those determined by Larson *et al.*² As expected, the neutron refinements give a much higher precision on the positions of the F atoms, and their temperature factors.

III. DISCUSSION

The unit cell of the AnF_4 compounds contains 12 U atoms and 48 F atoms. Four (An1) sites have C_2 symmetry and eight (An2) have C_s symmetry. The coordination of each An atom is eightfold in a distorted antiprism configuration. The most convenient way to represent the change in configuration with temperature is to consider the angles between the planes defined by three fluorine atoms at a time. We illustrate the relevant planes around the U atoms in Fig. 4. In Fig. 5(a) are shown the temperature dependence of the planes around the U1 atom. The small value of the angles between the

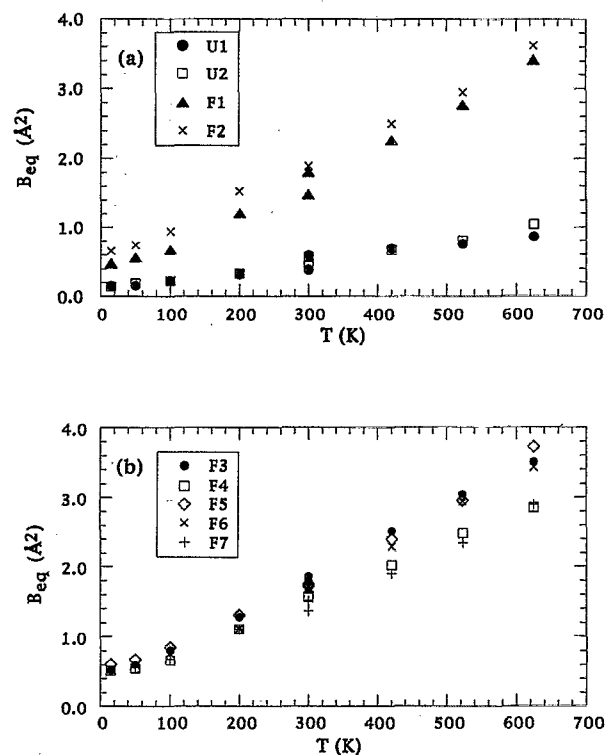


FIG. 3. Results for the isotropic equivalent temperature factors for UF_4 as a function of temperature. These have been derived from the anisotropic thermal parameters given by the least-squares analysis at each temperature.

planes indicates that for An1 the distortion from the antiprism configuration (in which the angle would formally be zero degrees) is small. Nor does it change appreciably with temperature. In the case of the An2 site the angles between planes 3 and 4 and 7 and 8 are as small as they are for An1; but the distortions between the planes 1 and 2 and (especially) 5 and 6 are significantly larger. As with the other planes the configuration tends to become more “regular” (i.e., the angles tend to zero) in a monotonic way with increasing temperature. The distances between the fluorines and the central An atom increase slowly and regularly with increasing temperature. However, the large value of the angles between the planes 1 and 2 and 5 and 6 [Fig. 5(b)] causes the configuration to be very distorted and to require a considerable amount of space in the structure. As the temperature increases from 15 K the distortion *decreases* in im-

TABLE II. Cell parameters for ThF_4 and NpF_4 at selected temperatures. Standard deviations are 2 in the least-significant digit.

	ThF_4 (15 K)	ThF_4 (300 K)	NpF_4 (300 K)
<i>a</i> (Å)	13.0572	13.0450	12.676
<i>b</i> (Å)	11.0205	11.0128	10.745
<i>c</i> (Å)	8.5437	8.5362	8.306
β (deg)	126.38	126.39	126.41
Vol. (Å ³)	989.82	987.24	910.5

TABLE III. Results of refinement of UF_4 neutron powder patterns at 300 K.^a The atomic coordinates (xyz) are multiplied by 10^4 . B_{eq} is the equivalent isotropic temperature factor derived from the anisotropic components of the temperature factor. The scattering lengths used were $b_{\text{U}}=0.8407$, $b_{\text{F}}=0.5654(\times 10^{-12} \text{ cm})$. In each case the first parameter is that found in this study, and the second that from Ref. 2. The standard deviations refer to the least-significant digit. On the temperature factors the standard deviations are $\sim 10\%$ of the values.

Atom	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
U1	0	0	2131(2)	0.39
U2	2044(1)	2042(2)	4277(1)	0.45
F1	2500	2500	2500	1.81
F2	0	0	6041(2)	1.89
F3	8935(2)	8843(26)	2937(2)	1.80
F4	8800(2)	8786(23)	543(2)	1.58
F5	7887(2)	7894(23)	5303(2)	1.75
F6	6182(2)	6192(24)	1211(2)	1.67
F7	6252(2)	6287(22)	3472(2)	1.51

^aIn the refinement using the Rietveld method the following R factors were found. $R(F^2)=4.59\%$, $R(P)=2.16\%$, $R(wP)=3.33\%$, $R(\text{Riet.})=6.23\%$, $R(\text{exp.})=1.62\%$. The number of reflections used was 9879.

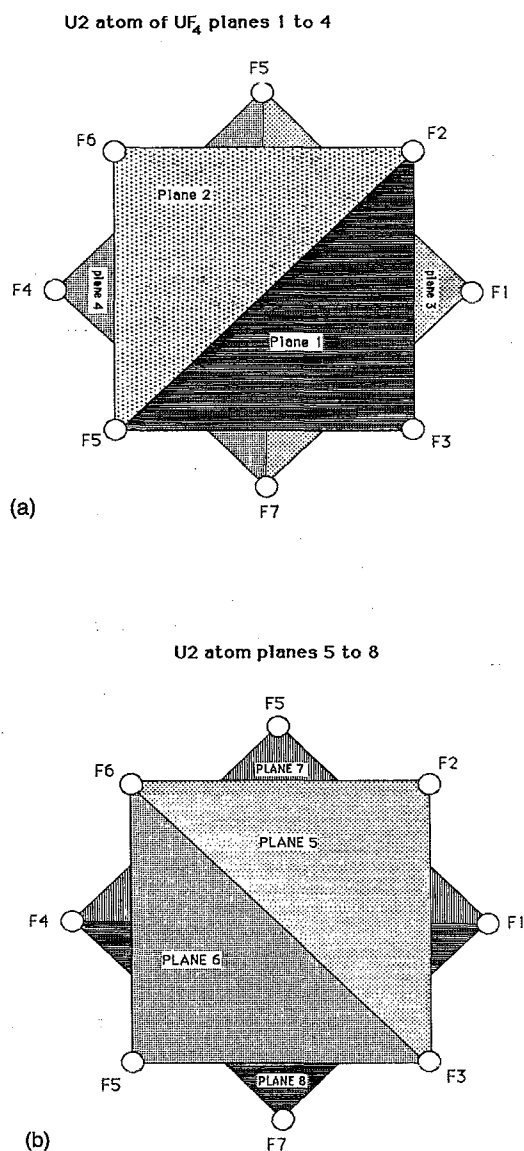


FIG. 4. Description of planes around the An atom as defined by three fluorine atoms at a time. The An atom is in the center in a distorted cubic antiprism configuration. (a) Planes 1 to 4 and (b) planes 5 to 8.

portance, the molecular packing is more regular and the volume decreases. Finally, at more elevated temperatures, the whole molecular unit expands causing the anticipated expansion of the volume at higher temperature. Thus it is the competition between the degree of distortion, or "puckering," of the antiprism configuration around the An2 site and the mo-

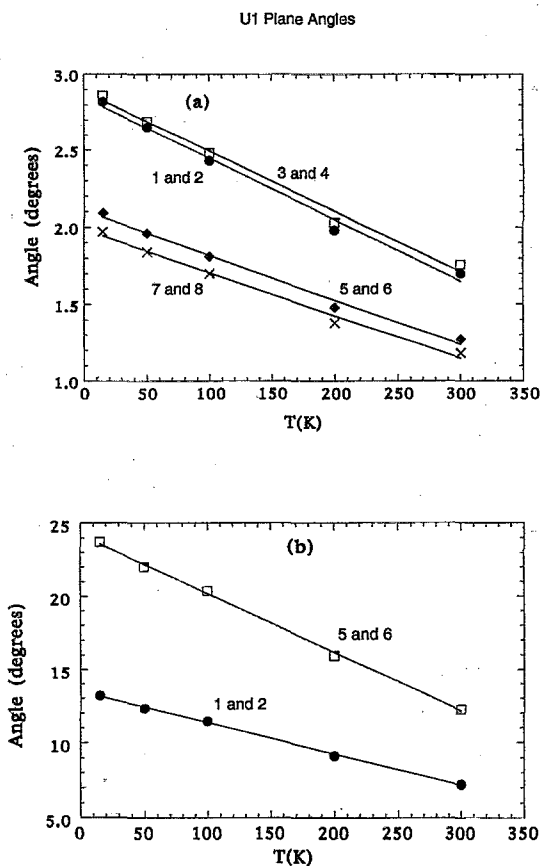


FIG. 5. Angles between the normals to the planes in degrees as a function of temperature around (a) the An1 site and (b) the An2 site. Note that for An2 the angles between the planes 3 and 4 and 7 and 8 are similar to those around An1, i.e., less than 3° .

lecular volume (i.e., the average interatomic distance) that causes the unusual behavior of the lattice parameters and the unit cell volume shown in Fig. 2.

IV. SUMMARY

The actinide tetrafluorides are isostructural with the monoclinic $C2/c$ space group. We have found an unusual volume dependence of UF_4 with a minimum at ~ 350 K. The lattice parameter of ThF_4 is also smaller at 300 than 15 K, and we assume that the same behavior is present; this implies that the cause of the volume dependence is lattice, rather than electronically, driven. An examination of the structural parameters for UF_4 as a function of temperature shows that there is a significant change in the configuration of the fluorine atoms around the An2 site. With lowering temperature the puckering of the ideal antiprism arrangement increases and is responsible for the unusual volume dependence. Why this distortion should change with temperature is not answered by our diffraction study.

ACKNOWLEDGMENTS

We would like to thank the staff at IPNS and the radiation safety personnel for assistance in running the transuranium sample at IPNS. We thank S. Dunn, S. Yarbrow, and S. Schreiber for purifying the NpO_2 prior to fluorination. IPNS is operated as a user facility by the USDOE. S.K., J.H., and S.R. thank IPNS and the Department of Educational Programs at Argonne for support during their stay at IPNS. J.W.R., F.J.R., and L.S. acknowledge funding from USDOE, BES-Chemical and Materials Sciences, under Contract No. W-31-109-Eng-38.

¹W. Zachariasen, *Acta Crystallogr.* **2**, 388 (1949).

²A. C. Larson, R. B. Roof, and D. T. Cromer, *Acta Crystallogr.* **17**, 555 (1964).

³W. T. Carnall, G. K. Liu, C. W. Williams, and M. F. Reid, *J. Chem. Phys.* **95**, 7194 (1992).

⁴S. Kern, G. H. Lander, L. Soderholm, C.-K. Loong, F. Trouw, M. West, D. Hoisington, B. Cort, and U. Welp, *J. Chem. Phys.* **101**, 9338 (1994).