gas phase above MF_5 and MF_4. Further studies of these vapors are warranted.

The infrared spectra listed in Table II show one common band in each compound: a broad absorption at about 530 cm^{-1}. From this work and earlier studies,[23] the assignment of the band as an M–F–M bridge mode appears to be certain. This band is further evidence for highly bridged polymeric structures of both the pentafluorides and tetrafluorides.

Registry No. ReF_5, 30937-52-1; ReF_4, 15192-42-4; OsF_5, 31576-40-6; OsF_4, 54120-05-7; IrF_5, 14568-19-5; IrF_4, 10025-97-5; ReF_6, 10049-17-9; OsF_6, 13768-38-2; IrF_6, 7783-75-7; Si, 7440-21-3; H_2, 1333-74-0; HF, 7664-39-3.

Supplementary Material Available. A listing of powder pattern *d* values for ReF_4, OsF_5, OsF_4, IrF_5, and IrF_4 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC40513T.

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Synthesis, Characterization, and Structure of Uranium Oxide Tetrafluoride[1]

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The synthesis of uranium oxide tetrafluoride from the combination of uranium hexafluoride and quartz wool (SiO_2) in anhydrous hydrogen fluoride solution is reported. The slow reaction $4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$ provides a stoichiometric, one-step, controlled, partial hydrolysis of UF_6. The characterization of UOF_4 including electronic and vibrational spectra of the solid is presented. The crystal structure as determined from three-dimensional single-crystal X-ray data collected by counter methods is described. A full-matrix least-squares refinement using 300 observed reflections resulted in a final $R = 4.2\%$. The structure refines in the trigonal space group $R3m$. The hexagonal cell constants are $a = 13.22$ (1) Å and $c = 5.72$ (1) Å with $V = 865.7$ cm^3, $d_c = 5.70$ g/cm^3, and $Z = 9$. The idealized coordination sphere of UOF_4 consists of a pentagonal bipyramid of light atoms surrounding the central uranium. An oxygen atom and fluorine atom occupy indistinguishable axial positions with the U–O and U–F distances in the range 1.77–1.79 (3) Å. The equatorial belt contains one unique unbridged fluorine ($U–F_{eq} = 1.98$ (3) Å) and four bridged fluorines ($U–F_{br} = 2.25–2.29$ (3) Å). The observed chemistry and structure are compared and discussed in relation to transition metal oxide tetrafluorides and previously reported uranium oxide fluorides.

Introduction

The simple yet important compound uranium oxide tetrafluoride, UOF_4, has had an uncertain history. It was first suggested by Brooks and coworkers[2] that UOF_4 might be the principal product of a gas-phase reaction of UF_6 with very low partial pressures of water. Surprisingly, their experiments indicated that, in the presence of excess hexafluoride, UF_6 and water combine in a 1:3 ratio to give a mixture of UO_2F_2 and $UO_2F_2{\cdot}2H_2O$. Bartlett and Robinson,[3] as part of a study of the fluorination properties of SeF_4, reported the formation of a cream-colored solid from the reaction of UO_3 and SeF_4. The compound analyzed as UOF_4. A subsequent reinvestigation of this reaction by Otey and LeDoux[4] was unsuccessful in producing UOF_4. In the same study, Otey and LeDoux, outlined a detailed investigation of the gas-phase, water-deficient hydrolysis of UF_6. They identified one new compound, $U_3O_5F_8$, and suggested the presence of an intermediate compound, $U_2O_3F_6$, but found no evidence for UOF_4. Until very recently, the synthesis of UOF_4 apparently received little further attention.

We previously reported a simple, high-yield synthesis of $ReOF_4$,[5] $MoOF_4$,[6] and WOF_4[6] from the controlled hydrolysis of the corresponding hexafluorides. Because of this success and the uncertainty surrounding the existence of UOF_4, we initiated a study of the controlled-hydrolysis chemistry of UF_6. During the course of our study two additional reports on syntheses of UOF_4 appeared. Wilson[7] and Jacob and Polligkeit[8] allowed UF_6 to react with dilute solutions of water in liquid HF. In each study an orange powder was collected and identified as UOF_4.

We report here a simple high-yield synthesis of UOF_4 from a solution-phase controlled-hydrolysis reaction. The synthesis is summarized by the equation

$$2UF_6 + SiO_2 \xrightarrow{\text{HF(l)}} 2UOF_4 + SiF_4$$

The UOF_4 was characterized, and the crystal structure was

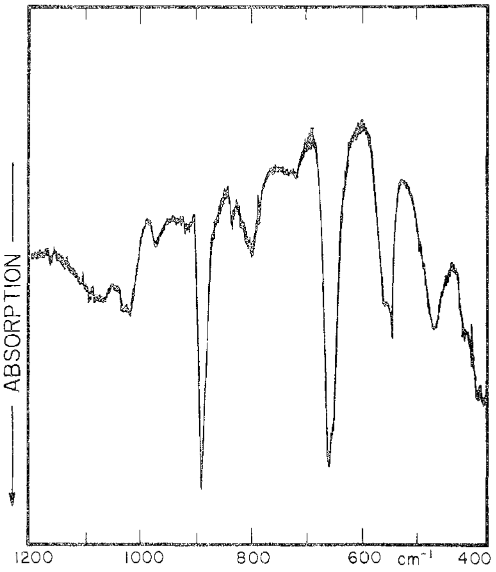

Figure 1. Infrared spectrum of finely powdered UOF_4 at 25°. The broad bands from 1150 to 1000 cm^{-1} and at 800 cm^{-1} are exterior window bands not associated with the compound.

determined by single-crystal X-ray diffraction methods.

Experimental Section

The manipulations of all volatile compounds were performed in a Monel vacuum line.[9] The reactions were contained in a 30-ml Kel-F reaction tube fitted with a high-pressure Monel valve. Depleted uranium hexafluoride was obtained from Oak Ridge National Laboratory and was used without purification. Hydrogen fluoride was purchased from Matheson Co. The crude HF was purified by trap to trap vacuum distillation, and the resulting liquid was stored over K_2NiF_6. Quartz wool was purchased from Baker Chemical Co. and was pretreated with hydrogen gas at *ca.* 400°. All manipulations of UOF_4 were performed in an inert-atmosphere drybox. Infrared spectra were recorded with a Perkin-Elmer 521 spectrophotometer (4000–400 cm^{-1}). A low-temperature infrared cell,[9] fitted with CsI exterior windows and thin AgCl interior plates in thermal contact with a liquid nitrogen cooled copper block, was used. The Raman spectra were recorded with a Cary 82 spectrometer using 6471-Å Kr^+ laser excitation. The Raman samples were contained in sealed thin-wall 5-mm glass nmr tubes. The electronic spectra were recorded with a Cary 14 spectrophotometer using the infrared cell described above, but fitted with sapphire windows. Mass spectra were recorded on a Bendix Model 12 time-of-flight mass spectrometer using a heated, solids-probe inlet system.

Preparation of UOF_4. In a typical reaction 91.7 mg (1.51 mmol) of quartz wool (SiO_2) and a Teflon-coated stir bar were placed in a Kel-F reaction tube, the tube was evacuated, and 10 ml of anhydrous HF was added. To this mixture 1.41 g (4.0 mmol) of UF_6 was added and the contents warmed slowly to room temperature. The stirred reaction was complete in 1–3 hr, and a fine yellow-orange powder (1.0 g, 100% yield based on SiO_2) was recovered. The powder was insoluble in the anhydrous HF, and it was insoluble in or it reacted with common organic solvents. The compound dissolved in water with formation of UO_2F_2.

Single crystals for X-ray diffraction analysis were grown under special conditions. A small, polished quartz rod 10 mm × 3 mm was placed in a Kel-F tube, and 15 ml of anhydrous HF and excess UF_6 were added. The tube was held undisturbed at 0° for 1–2 weeks. At the end of this time yellow-orange crystals coated the Kel-F tube. The crystals were chunky and shaped roughly as a cylinder with maximum dimensions of approximately 90 mm × 160 mm.

Characterization of UOF_4. The UOF_4 was chemically analyzed using a pyrohydrolysis technique.[10] The liberated HF was determined with a fluoride ion electrode. The uranium residue was ignited and determined as U_3O_8. A mass spectrum of the vapors above the solid at 100–150° was recorded at 70 eV and the principal ions are as follows [*m/e* (assignment) relative intensity]: 333 ($^{238}UF_5^+$) 100; 314 (UF_4^+) 28; 295 (UF_3^+) 26; 276 (UF_2^+) 25; 257 (UF^+) 21; 238 (U^+) 16. A gray powder remained in the probe crucible after heating. The infrared absorptions (cm^{-1}) from a powder sample at 25° are 895 m, sh, 891 vs, 885 s, sh, 658 s, 650 s, sh, 560 m, sh, 547 m, 472 m; the spectrum is shown in Figure 1. The Raman data (cm^{-1}) from a polycrystalline sample at 25° are 895 vs, 889 vs, 882 vs, 665 s, 658 s, 646 s, 550 m, 345 vw, 276 m, 201 m, 148 s, 117 m, 81 m, 59 w, 45 m. The spectrum is shown in Figure 2. An electronic spectrum of a mineral oil–UOF_4 mull at 25° shows only broad shoulders at *ca.* 450 and 400 nm on an end absorption.

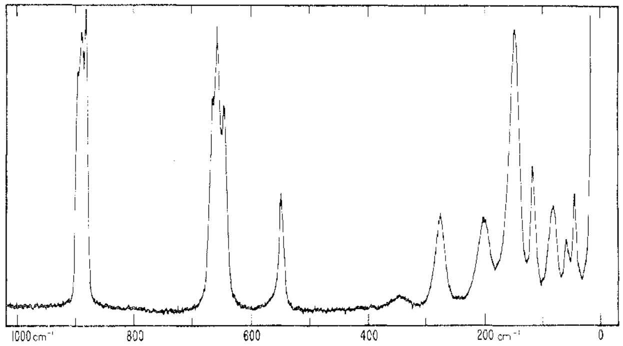

Figure 2. Raman spectrum of polycrystalline UOF_4 at 25°. The excitation frequency is 6471 Å.

X-Ray Data. Many of the crystals prepared above were either very small, twinned, or otherwise unsuitable for single-crystal X-ray study. A crystal fragment shaped roughly as a cylinder with dimensions 80 × 140 μ was selected and lodged in a glass capillary with a thin film of dry Kel-F grease. A sample of single crystals also was ground into a fine powder and powder X-ray photographs recorded. These photographs are identical with the photographs of the bulk powder material from the "fast" hydrolysis reaction.

Precession photographs (Mo Kα radiation) showed that the crystals were trigonal with systematic absences consistent with the space group $R\bar{3}m$ and its noncentric analogs $R32$ and $R3m$.

After alignment of the crystal on an automatic Picker four-circle diffractometer, 12 reflections with 2θ in the range 49–50° were centered (Mo Kα radiation). These positions were used in least-squares refinements of the cell parameters and the orientation matrices. The room-temperature unit cell constants and their standard deviations are $a = 13.22$ (1) and $c = 5.72$ (1) Å. The calculated cell volume is $V = 865.7$ cm^3 for $Z = 9$, and the calculated density is 5.70 g/cm^3. Density measurements could not be accomplished because of the extreme reactivity of the compound. Mosaicities of the crystals were checked by ω scans of several reflections.

One asymmetric unit of data (*i.e.*, all reflections of the type $hkil$ and $hki\bar{l}$) was collected using Mo Kα radiation, a 3° takeoff angle, and a graphite monochromator. Crystal data were collected to 70° in 2θ. A symmetric θ–2θ scan range of 2° was used and the scan rate was 1°/min. The background was counted for 20 sec at each end of the scan. Six hundred twenty-six reflections were measured, 600 of which satisfied the condition $I > 3\sigma(I)$. I is the intensity after background correction and $\sigma(I) = [(T + B) + [0.015(T - B)]^2]^{1/2}$ where T is the total count and B is the estimated background.[11] The intensities of standard reflections, counted after every 50 reflections, showed no significant change during data collection.

The data set was corrected for Lorentz and polarization effects and a relative absorption correction was made by deriving an empirical I *vs.* ψ curve from the $\bar{2}10$ reflection. An absorption correction using the Busing and Levy[12] method was not successful. The failure was probably due to the poor physical definition of the crystal planes and the large absorption coefficient. The linear absorption coefficient is 630 cm^{-1}, and the relative absorption varies by a factor of 2.5 as a function of ψ.

Refinement of Structure. The structure was solved using standard Patterson and Fourier techniques. The choice of $R3m$ as the correct space group was made on the basis of the physical reasonableness of possible solutions. The function $\sum w^2(|F_o| - |F_c{}^*|)^2$ was minimized[13] by full-matrix least-squares techniques.[14]

Neutral atom scattering factors[15] were used for all atoms and anomalous dispersion corrections were made for the uranium atom.[16] Attempts to resolve the structure in space groups $R\bar{3}m$ and $R32$ resulted in physically unreasonable models. The structure was refined in the noncentric space group $R3m$ to an unweighted R factor $R = \sum \| F_o| - |F_c\| / \sum |F_o|$ of 4.2%.[17] The final positional parameters,

Table I. Final Least-Squares Parameters for UOF_4[a]

Atom	x	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U
U[c]	0.86183 (5)	0.13817 (5)	0.0000 (0)	1.52 (4)	1.52 (4)	1.42 (5)	0.40 (5)	0.32 (3)	−0.32 (8)	
O[c]	0.4660 (11)	0.5340 (11)	0.1407 (47)							5.0 (6)
F_1[c]	0.5892 (10)	0.4108 (10)	0.5348 (46)							4.0 (6)
F_2	0.442 (13)	0.7550 (13)	0.9106 (25)							3.0 (3)
F_3[c]	0.2487 (13)	0.7513 (13)	0.3997 (57)							3.2 (9)

[a] In this and subsequent tables, the standard deviation in the last significant figure is given in parentheses. $g = 6.38 \times 10^{-8}$. [b] $U_{ij} = \beta_{ij}(A_i \times A_j)$ where β is defined in $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + \beta_{13}hk + \beta_{23}kl)]$ and A_i is the cell constant. [c] Postion 9(b), *i.e.*, x, $\bar{x}$, z.

temperature factors, and extinction coefficient g are given in Table I.

Inspection of Friedel-related reflections showed their variations to be well beyond that expected on the basis of anomalous dispersion effects, the discrepancy no doubt being due to the poor definition of the absorption. Three refinements were carried out: (a) refinement of either choice of the enantiomorph on the full data set using both real and imaginary anomalous dispersion components for the uranium atom and (b) refinement of the structure with only the real component of the anomalous dispersion on the data with Friedel pairs averaged. Refinement b was chosen to report here because both refinements of the unaveraged data resulted in a higher goodness of fit parameter, and the resulting distances and angles are not significantly different from each other or from those obtained in refinement b.

Discussion

Most hexafluorides and heptafluorides are known to undergo violent, total hydrolysis reactions in the presence of excess water. With a deficiency of water it might be expected that hydrolysis would occur in a stepwise fashion with the elimination of two fluorides and the addition of one oxide on the central atom in each step. If this is the case, then the isolation of intermediate oxide fluorides, MOF_4, MO_2F_2, etc., should be feasible. Indeed, an appropriately simple reaction summarized by the equation

$$2MF_{6,7} + SiO_2 \xrightarrow[HF(l)]{HF(trace)\ or} 2MOF_{4,5} + SiF_4$$

has been used to prepare the first-step hydrolysis products $XeOF_4$,[18] IOF_5,[19] $ReOF_4$,[5] $MoOF_4$,[6] and WOF_4.[6] The controlling step is the relatively slow reaction of quartz with HF which provides the required water in a stoichiometric amount.

The present study reveals that UF_6 is hydrolyzed smoothly in an SiO_2–HF slurry with the formation of UOF_4. The hydrolysis is continued to UO_2F_2 by simply starting with a UF_6:SiO_2 = 1 reactant ratio. The UOF_4 is a yellow-orange moisture-sensitive powder which noticeably decomposes on heating at about 200° under a static vacuum. The solid does not melt up to 200° and it is insoluble in anhydrous HF. These properties contrast those of the transition metal oxide tetrafluorides which are low melting and are soluble in anhydrous HF.[5,6] The compound has been characterized by chemical analysis, X-ray powder diffraction methods, and electronic, infrared, and Raman spectroscopy. All of the data are consistent with the molecular formula assignment UOF_4, and some details are worth discussion.

The analytical results are listed and compared in Table II with other known uranium oxide fluoride compositions. The experimental composition most closely agrees with the molecular formula UOF_4. The X-ray powder pattern from the bulk powder agrees with a calculated pattern obtained using the parameters found in the single-crystal study. A powder pattern from ground single crystals is in agreement with the pattern from the bulk material, which provides assurance that the bulk powder is identical with the material in the single crystal. The electronic spectrum from a mulled powder sample contains only two weak shoulders near 450 and 400 nm on top of a strong, continuous absorption beginning at about 550 nm. The electronic spectrum of UO_2F_2 in the same region, on the other hand, displays rich vibronic detail on the electronic transitions;[20,21] hence the yellow-orange solid of this study is definitely not UO_2F_2.

Table II. Composition and Analytical Data for Uranium Oxide Fluorides

Compd	% U	% F	F:U
	Theoretical Compositions		
UO_2F_2	77.3	12.3	2.0
$U_3O_5F_8$	75.5	16.1	2.67
$U_2O_3F_6$	74.6	17.9	3.0
UOF_4	72.1	23.0	4.0
UF_6	67.6	32.4	6.0
	Experimental Composition		
Orange Solid	71.0 ± 1.0	22.3 ± 0.4	3.9

On the basis of the observed cracking patterns of UF_6[22] and transition metal oxide tetrafluorides[5,6,23] the mass spectrum of UOF_4 would be expected to show a weak parent ion UOF_4^+ and a strong UOF_3^+ peak. Instead, no ions are detected with sample temperatures of 25–100°. Above 100° ions appear and the resulting spectrum is identical with the mass spectrum of UF_6.[22] A gray uranium oxide residue is left in the sample crucible. This result is consistent with the operation of an irreversible thermal decomposition of UOF_4 to UF_6 and an unidentified uranium oxide compound (U_3O_8?).

The infrared and Raman spectra of powdered UOF_4 are shown in Figures 1 and 2. Qualitatively the spectra are more complex and the bands sharper than those observed for solid transition metal oxide tetrafluorides. The infrared spectrum agrees with the spectrum reported recently by Jacob and Polligkeit.[8] The band at 891 cm^{-1} is assigned to a terminal U–O stretching mode on the basis of isotope shifts[8] and band position. It is important to note that this U–O stretch occurs at a significantly lower frequency than the asymmetric (ν_3) ir-active O–U–O stretch of most uranyl compounds (970–930 cm^{-1}),[24] but it agrees with the estimated Raman-active ν_1 of UO_2^+. Curiously the infrared band at 891 cm^{-1} was not reported by Wilson.[7] The two sharp bands at 658 and 547 cm^{-1} may be tentatively assigned to terminal U–F stretching modes and the broad bands at 472 and 375 cm^{-1} to U–F–U bridge modes. The Raman bands at 889, 658, and 550 cm^{-1} show excellent correspondence with the infrared absorptions. Lowering the sample temperature to −196° produced some additional sharpening in both spectra.

The characterization data, in particular the vibrational and mass spectra, suggested prior to the structure determination that the U–O group is clearly different from a classical uranyl UO_2^+ group, and the fluoride environments are part terminal and part strongly bridged. From this information it was anticipated that the structure would reveal several unique features as well as finally unambiguously confirm the existence of the compound.

The molecular structure of UOF_4 is depicted in Figure 3 and the pertinent interatomic distances and angles are listed in Table III. The idealized structure consists of a pentagonal bipyramid of light atoms surrounding the central uranium. The axial positions are occupied by atoms at 1.77 and 1.79 Å from the uranium. The pentagonal belt contains one terminal atom at a distance of 1.98 Å from the uranium and four bridging atoms at 2.25–2.29 Å.

Table III. Interatomic Distances (Å) and Angles (deg) in UOF_4

$U\text{–}X_{ax(1)}$	1.77 (3)	$U\text{–}F_3$	1.98 (3)
$U\text{–}X_{ax(2)}$	1.79 (2)	$U\text{–}F_{2-2}'''$	2.25–2.29 (2)
$X_{ax(1)}\text{–}U\text{–}X_{ax(2)}$	178.8 (12)	$F_2\text{–}U\text{–}F_3$	74.2
$X_{ax(1)}\text{–}U\text{–}F_2$	88.9 (5)	$F_2\text{–}U\text{–}F_2'$	69.5 (6)
$X_{ax(1)}\text{–}U\text{–}F_2'$	89.1 (6)	$F_2'\text{–}U\text{–}F_2''$	72.5 (8)
$X_{ax(1)}\text{–}U\text{–}F_3$	90.5 (12)	$U\text{–}F_2\text{–}U'$	153.2 (3)

Table IV. Nonbonded Contact Distances (Å) for UOF_4

$X_{ax(1)}\text{–}F_3$	2.67 (4)	$F_3\text{–}F_2$	2.59
$X_{ax(1)}\text{–}F_2$	2.84 (3)	$F_2\text{–}F_2'$	2.59
$X_{ax(1)}\text{–}F_2'$	2.87 (3)	$F_2'\text{–}F_2''$	2.66

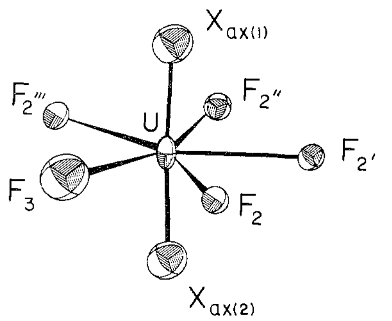

Figure 3. Local environment of the uranium atom in UOF_4.

The nonbridge equatorial distance, 1.98 Å, is in good agreement with the U–F distance in UF_6 and the position in question can clearly be assigned to a fluorine atom. The nonbonded contact distances in UOF_4 are listed in Table IV.

It is especially interesting that the oxygen atom takes the axial position in this structure since it has been shown that a similar coordination situation exists for the MOF_4 structures with M = Mo, W, Te, Re, and Xe.[6,25-27] The only known exception is SOF_4[28] which has the expected C_{2v} symmetry.

The [001] projection of the trigonal unit cell is shown in Figure 4. The molecular units are connected in hexameric trigonal arrays and the packing is dominated by the extensive uranium–fluorine bridging interactions. A [100] projection reveals that the trigonal arrays are stacked in layers which are cross-linked by U–F–U bridge bonds.

In summary, the molecular structure of UOF_4 as shown in Figure 3 is unique in transition and actinide metal oxide fluoride structures. This structure is the only known example of a pentagonal-bipyramidal array of light atoms in which there are axial and equatorial *nonbridged* fluorines and axial oxygen and fluorine. The crystal and molecular structures also are in clear agreement with the complementary physical characterization data presented here.

There is usually some ambiguity in the placement of an oxygen atom position with reference to fluorine atom positions in a molecular structure determined by X-ray diffraction methods. In most cases a final assignment must be made with the help of supporting physical characterization data and chemical intuition. The solution of the structure of UOF_4 is no exception.

We have concluded that the oxygen atom resides at a terminal, axial position on the basis of three observations. First, the oxygen is not bridging since vibrational spectra show no evidence for U–O–U vibrations, but rather a single strong U–O band at 885–881 cm^{-1}. Second, in all structure determinations to date on uranyl fluorides the U–O bond distance is found to be short (1.74–1.76 Å) and unbridged.[29-31] Although no other uranium oxide fluoride structure has been reported to have both terminal oxygen and terminal fluorine atoms, it is reasonable to assume that one of the two short distances belongs to the U–O bond. The observed bridging distances of 2.25–2.29 Å fall within the range 2.24–2.43 Å characteristic of most known bridging uranium fluoride distances.[29b,30,32] With limitations imposed by the data set quality, U–O and $U\text{–}F_{ax}$ labels cannot be uniquely fixed to either of the measured terminal distances $U\text{–}X_{ax(1)}$ and $U\text{–}X_{ax(2)}$ and, in fact, these distances are probably more inducive of disorder in these positions. It should be pointed out that the axial U–X distances of 1.77 or 1.79 Å are much shorter than observed in UF_6 (U–F = 1.99 Å)[33] where the F–F distances are all contact distances.

Assuming that the axial positions are a result of disorder between an oxygen and a fluorine atom the average axial distance is considerably shorter than one would expect from averaging a "normal" U–F distance (1.99 Å) and a uranyl distance. It should be noted, however, that no accurate distance has been established for this type of uranyl bond (in β-UOF_4 the oxygen atom is in the equatorial plane; see below). Furthermore, nonbonded F–F repulsions are expected to be less for a F atom in the axial position of a pentagonal bipyramid than one at the corner of an octahedron (*i.e.*, note the longer than normal F–F contact distances in this structure for the axial position). The U–F axial distance should be shorter therefore than in UF_6. The short axial distances in this study indicate however a U–O distance considerably shorter than that found in β-UOF_4.

During the course of the preparation of this article a communication on a structure determination of β-UOF_4 by Taylor and Wilson[34] appeared. It was suggested by the authors that their original UOF_4 sample[7] has a different crystal form (α-UOF_4). The β-UOF_4 is isostructural with β-UF_5 and is tetragonal, space group $I\bar{4}2d$. Their molecular structure also consists of a pentagonal bipyramid of light atoms around the uranium. In their structure, however, the atomic positions have been assigned to *two* nonbridging axial fluorines (U–F = 1.92 Å), a nonbridging *equatorial* oxygen (U–O = 1.87 Å), and four equatorial bridging fluorines (U–F = 2.18 Å). This structure is clearly different from that described in our study and our structure may correspond to their α-UOF_4 compound.

Registry No. UF_6, 7783-81-5; SiO_2, 7631-86-9; HF, 7664-39-3; UOF_4, 39630-96-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition

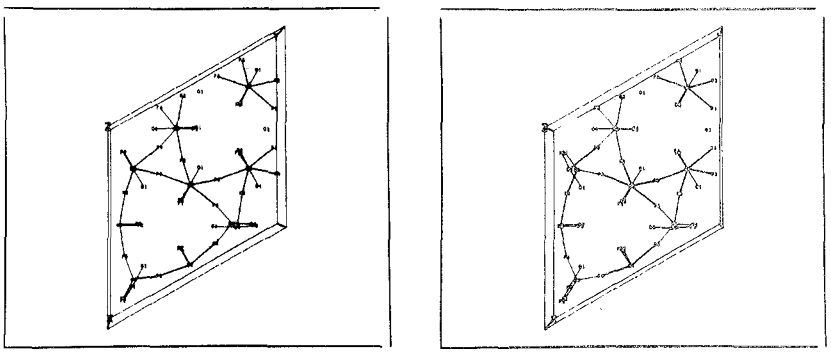

Figure 4. Stereoview of the unit cell contents, [001] projection.

of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC403814.

References and Notes

(1) This work was performed under the auspices of the U.S. Atomic Energy Commission. The crystal structure was initially reported at the American Crystallographic Association Meeting, March 1974; see Abstract No. F2.
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Diffusionless Orthorhombic to Hexagonal Transitions in Ternary Silicides and Germanides

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Stoichiometric MnCoGe and MnNiGe are orthorhombic, ordered Co_2P type at room temperature and not hexagonal Ni_2In type as previously reported. These germanides and the corresponding silicides transform diffusionlessly at elevated temperatures to the hexagonal Ni_2In structure. For the germanides, the orthorhombic to hexagonal transition temperature changes rapidly with small compositional changes. These transitions (*Pnma* to *P*6₃/*mmc*) like those between closely related MnP and NiAs structures are ferroelastic. The crystallographic, phase analytical, and magnetic properties of hexagonal and orthorhombic forms presented suggest the importance of metal–metal bonding to the relative stability of these structures.

Introduction

MnCoGe and MnNiGe were first reported[1] to have the hexagonal Ni_2In structure. Powder patterns of MnCoSi and MnNiSi[2,3] were indexed as orthorhombic, ordered Co_2P type.[4,5] (This orthorhombic structure is also described as anti-$PbCl_2$ or TiNiSi type. Here we use ordered Co_2P type to emphasize relationships with the MnP and "filled-NiAs" (Ni_2In) type.) Magnetic properties were reported[6] for the germanides. Only Austin[7] identified crystallographic transitions in compositions close to MnCoGe and MnNiGe.

Contrary to most reported results, we find all four phases, MnCoSi, MnNiSi, MnCoGe, and MnNiGe, to be isostructural at room temperature with the orthorhombic, ordered Co_2P-type structure if compositions are maintained close to equiatomic. They all transform to the hexagonal Ni_2In structure at elevated temperatures. We describe here preparation, crystallographic and magnetic properties, and some phase analytical results for compositions close to MnCoGe.

Experimental Section

Sample Preparation. MnCoSi and MnNiSi were prepared as described elsewhere.[8]

MnCoGe and MnNiGe were prepared from high-purity elements (99.999%) in Al_2O_3-lined silica tubes between 800 and 1050°. An Al_2O_3 liner is necessary to prevent reaction with the silica tube which drastically alters the nominal stoichiometry. In a typical reaction, 99.999% Mn (purified by partial sublimations), 99.999% Co powder (H_2 reduced), and intrinsic grade Ge in the atomic ratio 1:1:1 were sealed under vacuum in an Al_2O_3-lined silica tube, fired at 975° for 16 hr and slowly cooled. (The weight loss after this firing step was 0.086%, which, assuming only Mn losses, corresponds to the composition $Mn_{0.997}CoGe$.) The sample was then crushed, resealed in another Al_2O_3-lined silica tube, fired at 1050° for 2 hr, cooled to 700°, held for 16 hr, and cooled quickly. The resulting ingot shattered on cooling to room temperature. (The weight loss at this stage was 0.396%, which, again assuming only Mn losses and neglecting mechanical losses, corresponds to $Mn_{0.987}CoGe$.) Similar procedures were used for the preparation of other compositions close to MnCoGe and MnNiGe.

Structural Studies. Room-temperature *d* values were measured by the Hägg-Guinier X-ray powder diffraction technique. Cell dimensions were obtained by least-squares refinement.

Several high-temperature X-ray powder techniques were used to study the structural transformations. Powder diffractometry under dry helium in a Tempres camera and a GE diffractometer was used for MnCoSi. Patterns (Cr radiation) were recorded according to the following sequence: 25, 800, 900, 975, 900, 800, and 25°. In a second experiment, powder patterns of MnCoSi were obtained at 25 and