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Crystal Chemical and Thermodynamic Study on $CaUO_{4-x}$, $(Ca_{0.5}Sr_{0.5})UO_{4-x}$, and α-$SrUO_{4-x}$ ($x = 0 \sim 0.5$)

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A crystallographic and thermochemical study of $CaUO_{4-x}$, $(Ca_{0.5}Sr_{0.5})UO_{4-x}$, and α-$SrUO_{4-x}$ with x values ranging from nearly 0 to 0.5 was carried out. As the crystal radius of the divalent cations increases, a(rhomb) of nearly stoichiometric compounds increases, accompanied by an increase in the cell volume, whereas α(rhomb) decreases. With nonstoichiometry, the lattice parameters of $(Ca_{0.5}Sr_{0.5})UO_{4-x}$ and α-$SrUO_{4-x}$ discontinuously change at $4 - x = 3.79$ and 3.77, respectively, although each compound is a single phase in the entire range from $4 - x = 4.00$ to 3.50. For $CaUO_{4-x}$, the products were two-phase mixtures between $4 - x = 3.98$ and 3.70. These crystal structures are discussed taking into account the lattice parameters and interatomic distances. In the nonstoichiometric crystals, oxygen vacancies exist on the O_{II} sites but not on the O_I sites. The enthalpy of formation of α-$SrUO_{4-x}$ was measured for several specimens with different x values by solution calorimetry, and was expressed in a second-order polynomial of x by least-squares calculation. This quantity and its derivative, i.e., partial molar enthalpy of oxygen, suggest the change of defect species with x and the existence of repulsive vacancy–vacancy interaction. © 1993 Academic Press, Inc.

Introduction

The crystal structures of alkaline-earth monouranates $MeUO_4$ (Me = Mg, Ca, Sr, and Ba) differ. In $CaUO_4$ and α-$SrUO_4$ crystals, each uranium atom is surrounded by six O_{II} atoms forming a trigonal antiprism with two O_I atoms perpendicular to the trigonal planes (*1*). In $MgUO_4$, β-$SrUO_4$, and $BaUO_4$ crystals, on the other hand, two O_I atoms and four O_{II} atoms are located around each uranium atom forming a distorted octahedron (*2, 3*). $CaUO_4$ and α-$SrUO_4$ are rhombohedral with space group $R\bar{3}m$ (*1*), while β-$SrUO_4$ and $BaUO_4$ are orthorhombic with space group $Pbcm$ (*2*). $MgUO_4$ also crystallizes in an orthorhombic system, but its space group is $Imma$ (*3*).

It is interesting that only the rhombohedral-type monouranates, $CaUO_4$ and α-$SrUO_4$, have a wide range of oxygen nonstoichiometry, i.e., $CaUO_{4-x}$ and α-$SrUO_{4-x}$ with x values up to nearly 0.5 (*4–7*). When α-$SrUO_4$ is held in air or oxygen atmosphere and the temperature is raised at a 2 K · min^{-1} rate, it loses oxygen, resulting in formation of the nonstoichiometric monouranate above 773 K, but it rapidly transforms into nearly stoichiometric β-$SrUO_4$ on passing through the transformation temperature 1053 K (*4*). On the other hand, no such transformation occurs for $CaUO_4$, which is of course due to nonexistence of the β-$SrUO_4$ type modification for $CaUO_4$, but the crystal chemical background around these problems does not

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seem to have been fully resolved. Crystal structures, thermodynamic properties, thermal stabilities, etc., of stoichiometric $CaUO_4$ and α-$SrUO_4$ have been reported (*1, 2, 4–14*). The standard enthalpies of formation and the specific heats have been measured by O'Hare *et al.* (*12*), Cordfunke and Loopstra (*6*), and Leonidov (*13*). The thermal stabilities have been also studied by Wisnyi and Pijanowski (*14*). However, these studies do not pay full attention to the oxygen nonstoichiometry and the difference between calcium and strontium in $MeUO_4$ (*Me* = Ca and Sr).

In this study, the crystal chemical and thermodynamic properties of $CaUO_{4-x}$ and α-$SrUO_{4-x}$ were investigated by X-ray diffraction and solution calorimetry for x values from nearly 0 to 0.5. The effect of the crystal radius difference between Ca^{2+} and Sr^{2+} and the partial molar enthalpy of O_2 in $SrUO_{4-x}$ are discussed.

Experimental

1. Sample Preparation

Calcium monouranate, $CaUO_4$, was prepared by heating an intimate mixture of $CaCO_3$ (purity 99.995%, Aldrich Chemical Co.) and UO_2 with a Ca/U atom ratio of unity in air at 1273 K for 48 hr. The mixing and heating process was repeated three times until a completely homogeneous product was obtained, as determined by X-ray powder diffraction. The UO_2 was made by reducing U_3O_8, which had been prepared by air oxidation of high purity uranium metal (*15*), in a stream of hydrogen at 1273 K for 15 hr. $CaUO_{3.5}$ was prepared by reducing $CaUO_4$ in a stream of hydrogen at 1073 K for 6 hr. This temperature is because $CaUO_{3.5}$ is reported to decompose above 1173 K in a hydrogen atmosphere (*7*).

For preparing rhombohedral α-$SrUO_4$ and α-$SrUO_{3.5}$, orthorhombic β-$SrUO_4$ was first prepared by heating a mixture of $SrCO_3$ (purity 99.995%, Aldrich Chemical Co.) and UO_2 in air at 1273 K for 48 hr. The lattice parameters of the β-$SrUO_4$ were a = 5.4889 ± 0.0004, b = 7.9766 ± 0.0006, and c = 8.1302 ± 0.0006 Å, in good agreement with the literature values, a = 5.4890, b = 7.9770, and c = 8.1297 Å (*2*). α-$SrUO_{3.5}$ was prepared by reducing the β-$SrUO_4$ in a stream of hydrogen at 1073 K for 6 hr. α-$SrUO_4$ was obtained by heating α-$SrUO_{3.5}$ in air at 773 K for 6 hr. This temperature was low enough to avoid the transition of α-$SrUO_4$ to β-$SrUO_4$ (*4*).

$MeUO_{4-x}$ (*Me* = Ca and Sr) with various x values between 0 and 0.5 were prepared by heating the calculated amounts of the mixtures of $MeUO_4$ and $MeUO_{3.5}$ in vacuum-sealed quartz ampoules at 1273 K for 10 hr.

Quaternary rhombohedral monouranates, $(Ca_{0.5}Sr_{0.5})UO_{4-x}$, were prepared from $MeUO_4$ and $MeUO_{3.5}$ (*Me* = Ca + Sr in 1 : 1 atom ratio) as above. Since $(Ca_{0.5}Sr_{0.5})UO_4$ does not have the β-$SrUO_4$ type modification, it was prepared by heating the mixture of $CaCO_3$, $SrCO_3$, and UO_2 (Ca : Sr : U = 1 : 1 : 2) in the same way as the $CaUO_4$ preparation.

The oxygen-deficient samples ($x > 0$) were handled in a dry box filled with high purity nitrogen to avoid oxidation.

2. Determination of Oxygen Nonstoichiometry

The oxygen nonstoichiometry x in $MeUO_{4-x}$ (*Me* = Ca, Sr, and $Ca_{0.5}Sr_{0.5}$) was determined by a cerium back titration method (*16, 17*): In the dry box, a sample (ca.20 mg) was precisely weighed and put into a small glass vessel. In order to protect the sample from reaction with air oxygen, the vessel was sealed with Parafilm. Immediately after being taken out of the dry box, the sample was dissolved in excess Ce(IV) sulfate solution, which had been standardized using stoichiometric UO_2 beforehand. The excess Ce(IV) was titrated against Fe(II) ammonium sulfate solution using ferroin indicator. The error in the determined x values is estimated to be ±0.003.

3. X-Ray Diffraction Measurements

To determine the lattice parameters, Debye–Scherrer patterns of the powdered

samples in a vacuum-sealed capillary were taken with a Norelco 114.6-mm camera using nickel-filtered Cu$K\alpha$ radiation. The lattice parameters were calculated by a least-squares method including the Nelson–Riley extrapolation technique (*18*) with the use of the LCR-2 program.

A diffractometer was used for structure analyses of the samples. To prevent a powder sample from oxidizing during measurement, the sample plate was covered with an aluminized Mylar film which satisfactorily passed the X-rays but prevented the passage of gases. Diffraction patterns were taken with a Rigaku Geigerflex-CN2182 diffractometer using Cu$K\alpha$ radiation monochromatized with a curved pyrolytic graphite placed between the sample and the NaI(Tl) scintillation detector. The slit system used was 0.5°–0.1 mm–0.5°. For each specimen, the integrated intensities of about 45 reflections were collected by the step-scanning mode ($2\theta < 110°$). The diffraction angles were corrected using a silicon standard.

4. *Enthalpy of Formation of α-$SrUO_{4-x}$*

The enthalpy of formation of α-$SrUO_{4-x}$ at 298 K was obtained from the heat of solution of the samples in 5.94 *M* HCl. This medium dissolves α-$SrUO_{4-x}$ within 4 min without oxidizing U(IV) or reducing U(VI), although it does not dissolve $CaUO_{4-x}$ at an acceptable rate for calorimetry. The details for apparatus and procedure have been described elsewhere (*19*).

Crystal Structure Analyses

In the reflected peaks of the samples, no systematic absences were observed, confirming the space group to be $R\bar{3}m$ as reported by Zachariasen (*1*). The atomic positions are 1U on 1*a* (0, 0, 0), 1*Me* (*Me* = Ca, Sr, and $Ca_{0.5}Sr_{0.5}$) on 1*b* (1/2, 1/2, 1/2), $2O_I$ on 2*c* $\pm(u, u, u)$, and $2O_{II}$ on 2*c* $\pm$ (v, v, v) in the rhombohedral setting. Intensity analyses were carried out for nearly stoichiometric $CaUO_{3.981}$, α-$SrUO_{3.978}$, and $(Ca_{0.5}Sr_{0.5})UO_{3.967}$, as well as highly nonstoichiometric α-$SrUO_{3.777}$ and α-$SrUO_{3.597}$.

The two oxygen-positional parameters, u and v, for nearly stoichiometric $MeUO_4$ were determined by minimizing the *R*-value

$$R = \Sigma w\,|I_{obs} - I_{calc}|/\Sigma w I_{obs}, \qquad (1)$$

where I_{obs} and I_{calc} are the observed and calculated intensities, respectively. The I_{calc} was calculated using the LAZY-PULVERIX program (*20*) on a FACOM-M780 computer. The weight, w, was regarded to be $w = I_{obs}^{-1}$ for $I_{obs} \geqq 10 \cdot I_{obs}$ (minimum) and $w = [10 \cdot I_{obs}\,(\text{minimum})]^{-1}$ for $I_{obs} < 10 \cdot I_{obs}\,(\text{minimum})$. No correction was made for the thermal motion. The atomic scattering factors used in the calculation were those from Tokonami (*21*) for O^{2-} and from Cromer and Waber (*22*) for Sr^{2+}, Ca^{2+}, and U^{6+} with anomalous dispersion corrections (*23*). In Fig. 1, the variation of the *R*-value with varying u and v is shown for α-$SrUO_{3.978}$ as an example. The values of u and v for nonstoichiometric α-$SrUO_{4-x}$ were obtained by a similar procedure. For these samples, however, it was necessary to incorporate the oxygen occupation factor, z, since the large deficiency of oxygen causes a change in the X-ray peak intensities. This factor, which is defined as the number of O_I atoms per chemical formula of the monouranate at a given nonstoichiometry, was refined together with u and v by minimizing the *R*-value. The distribution of vacancies within each of the O_I and O_{II} sites was considered to be random.

Results and Discussion

1. *Lattice Parameters and Atomic Parameters of Stoichiometric $MeUO_4$*

A three-dimensional view of the arrangements of the oxygen atoms around the uranium and the alkaline-earth metal atoms is shown in Fig. 2. The uranium atoms are located on the planes normal to the hexagonal *c* axis, the separation of the planes being *c*(hex)/3. Around one uranium atom there

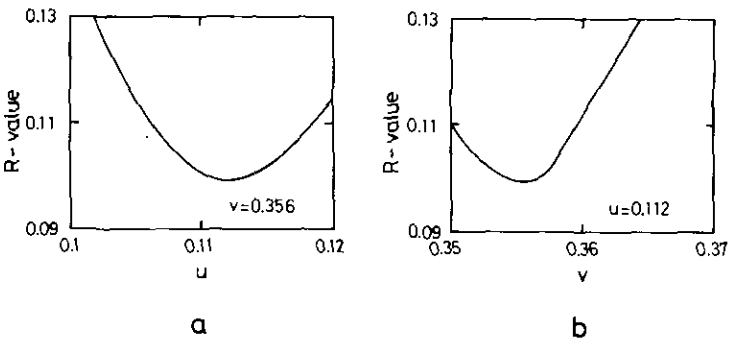

FIG. 1. Variation of R-value for α-$SrUO_{3.978}$ (a) as a function of u parameter with v fixed at 0.356; (b) as a function of v parameter with u fixed at 0.112.

are six O_{II} atoms, three of which are on the plane above and three on the plane below the plane of the uranium atoms, and two O_I atoms are situated on the line normal to the uranium plane. Arrangements around the alkaline-earth metal atom can be written similarly if O_{II} is changed to O_I, and O_I to O_{II}.

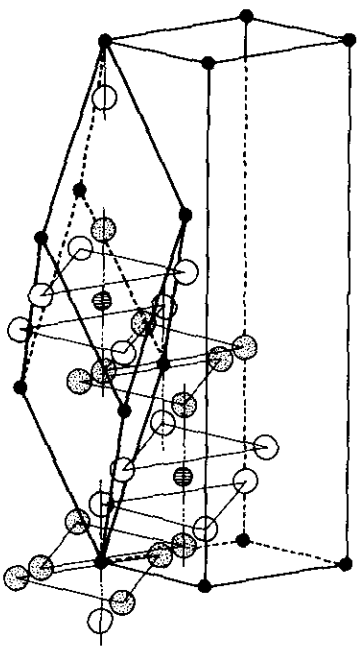

FIG. 2. Perspective view of rhombohedral cell showing arrangements of oxygen atoms around uranium and alkaline-earth metal atoms: (●) U; (⊜) *Me*; (○) O_I; (◎) O_{II}.

The lattice parameters and the interatomic distances of nearly stoichiometric $MeUO_4$ (*Me* = Ca, Sr, and $Ca_{0.5}Sr_{0.5}$) are shown in Table I, together with those of earlier reports. The values for $CaUO_4$ are in good agreement with those reported in Refs. (*1*) and (*2*). For α-$SrUO_4$, the present data are significantly discrepant from the values of Zachariasen (*1*), while in good agreement with those of Ref. (*9*). Zachariasen prepared the α-$SrUO_4$ by adding U_3O_8 or UO_3 to an excess of molten $SrCl_2$ at 1273 K. This method of preparation is less reliable than that used in this study. As described later, the lattice parameters and the interatomic distances of the "α-$SrUO_4$" of Ref. (*1*) are consistent with those of our α-$SrUO_{3.777}$ (Table II). Therefore, it is possible that the "α-$SrUO_4$", the composition of which was not analyzed, is markedly nonstoichiometric.

The lattice parameters, a(hex) and c(hex), of α-$SrUO_4$ are larger than those of $CaUO_4$, consistent with the larger crystal radius of Sr^{2+}. The lattice parameters of $(Ca_{0.5}Sr_{0.5})UO_4$ are almost identical to the means of the lattice parameters of $CaUO_4$ and α-$SrUO_4$; i.e., a(hex) = 3.900 and c(hex) = 18.003 Å.

Expressing the above three monouranates as $Ca_{1-y}Sr_yUO_4$, we have plotted the interatomic distances between the metal and

TABLE I

LATTICE PARAMETERS AND INTERATOMIC DISTANCES OF NEARLY STOICHIOMETRIC $MeUO_4$

	$CaUO_4$			α-$SrUO_4$			$(Ca_{0.5}Sr_{0.5})UO_4$
	This work	Zachariasen (*1*)[a]	Loopstra and Rietveld (*2*)[a]	This work	Zachariasen (*1*)[a]	Fujino *et al.* (*9*)	This work
Composition	$CaUO_{3.981(2)}$	—	—	$SrUO_{3.978(1)}$	—	$SrUO_{3.948}$	$(Ca_{0.5}Sr_{0.5})UO_{3.967(3)}$
a(hex) /Å	3.877(1)	3.876	3.878	3.922(1)	3.993	3.921	3.899(1)
c(hex) /Å	17.560(5)	17.56	17.564	18.446(5)	18.37	18.443	18.033(5)
c/*a*(hex)	4.529(2)	4.530	4.529	4.703(2)	4.601	4.704	4.625(2)
a(rhomb) /Å	6.267(3)	6.267	6.268	6.552(3)	6.543	6.551	6.419(3)
α(rhomb) /°	36.04(2)	36.03	36.04	34.83(2)	35.53	34.83	35.36(2)
V(rhomb) /Å^3	76.19(5)	76.15	76.25	81.90(5)	84.55	81.85	79.13(5)
u	0.111(2)	0.109	0.112	0.112(2)	0.104	0.112	0.111(2)
v	0.363(2)	0.361	0.363	0.356(2)	0.357	0.357	0.358(2)
U–O_I /Å	1.95(4)	1.91	1.97	2.07(4)	1.91	2.07	2.00(4)
U–O_{II} /Å	2.30(1)	2.29	2.30	2.30(1)	2.35	2.30	2.29(1)
Me–O_I /Å	2.44(2)	2.46	2.44	2.48(2)	2.58	2.48	2.47(2)
Me–O_{II} /Å	2.41(4)	2.44	2.41	2.66(4)	2.63	2.64	2.56(4)
O_I plane /Å[b]	±0.98(4)	±1.01	±0.96	±1.01(4)	±1.15	±1.01	±1.00(4)
O_{II} plane /Å[c]	±0.52(4)	±0.49	±0.52	±0.42(4)	±0.44	±0.43	±0.45(4)
O_I–O_I /Å	2.97(5)	3.02	2.95	3.03(5)	3.26	3.03	3.02(5)
O_I–O_{II} /Å	2.66(4)	2.66	2.67	2.80(4)	2.74	2.79	2.74(4)
O_{II}–O_{II} /Å	2.47(3)	2.44	2.47	2.41(3)	2.46	2.42	2.42(3)

Note. The values in parentheses are the standard deviations.

[a] Interatomic distances are recalculated from the literature values of lattice parameters *a*(hex) and *c*(hex), and atomic parameters of oxygen *u* and *v*.

[b] Separation of O_I plane from *Me* plane.

[c] Separation of O_{II} plane from U plane.

the oxygen atoms against *y*. The result is shown in Fig. 3. The distances between the metal (U and *Me*) and the six oxygen atoms that are in the two horizontal planes slightly above and below the metal (Fig. 2), giving rise to U–O_{II} and *Me*–O_I bonds, do not change with *y*. The U–O_{II} bond lengths are close to the sum of the crystal radii of U^{6+} and O^{2-} (*24*) shown by the dotted line in Fig. 3. On the other hand, the distances of the U–O_I and *Me*–O_{II} axial (parallel to the

TABLE II

LATTICE PARAMETERS AND INTERATOMIC DISTANCES OF α-$SrUO_{4-x}$

Composition	α-$SrUO_{3.978(1)}$	α-$SrUO_{3.777(1)}$	α-$SrUO_{3.597(1)}$
a(hex) /Å	3.922(1)	3.994(1)	3.995(1)
c(hex) /Å	18.446(5)	18.368(5)	18.511(5)
c/*a*(hex)	4.703(2)	4.599(2)	4.634(2)
a(rhomb) /Å	6.552(3)	6.543(3)	6.587(3)
α(rhomb) /°	34.83(2)	35.54(2)	35.30(2)
V(rhomb) /Å^3	81.90(5)	84.58(5)	85.28(5)
u	0.112(2)	0.101(2)	0.104(2)
v	0.356(2)	0.356(2)	0.352(2)
U–O_I /Å	2.07(4)	1.86(4)	1.93(4)
U–O_{II} /Å	2.30(1)	2.34(1)	2.33(1)
Sr–O_I /Å	2.48(2)	2.60(2)	2.58(2)
Sr–O_{II} /Å	2.66(4)	2.65(4)	2.74(4)
O_I plane /Å[a]	±1.01(4)	±1.21(4)	±1.16(4)
O_{II} plane /Å[b]	±0.42(4)	±0.42(4)	±0.35(4)
O_I–O_I /Å	3.03(5)	3.34(5)	3.27(5)
O_I–O_{II} /Å	2.80(4)	2.72(4)	2.80(4)
O_{II}–O_{II} /Å	2.41(3)	2.45(3)	2.41(3)

Note. The values in parentheses are the standard deviations.

[a] Separation of O_I plane from Sr plane.

[b] Separation of O_{II} plane from U plane.

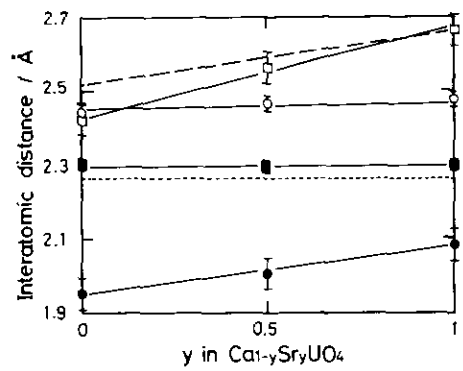

FIG. 3. Interatomic distances as a function of *y* in $Ca_{1-y}Sr_yUO_4$: (●) U–O_I; (■) U–O_{II}; (○) *Me*–O_I; (□) *Me*–O_{II}; (---) sum of crystal radii of U^{6+} and O^{2-} (*24*); (– – –) sum of crystal radii of Me^{2+} and O^{2-} (*24*).

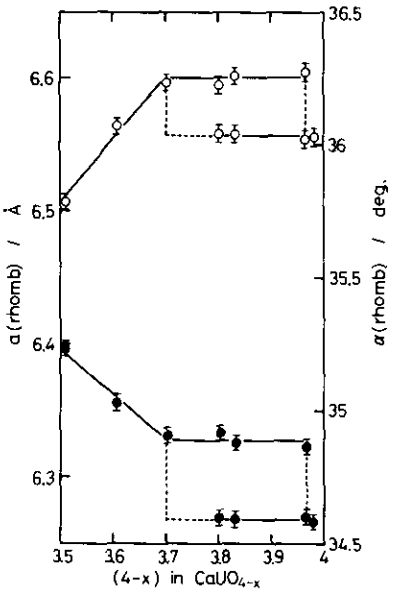

FIG. 4. Lattice parameters as a function of $4 - x$ in $CaUO_{4-x}$: (●) a(rhomb); (○) α(rhomb).

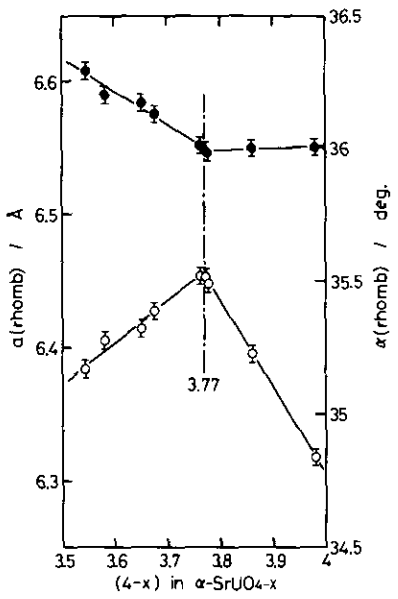

FIG. 5. Lattice parameters as a function of $4 - x$ in α-$SrUO_{4-x}$: (●) a(rhomb); (○) α(rhomb).

hexagonal axis) bonds increase nearly linearly with increasing y. The increase in the Me–O_{II} length can be qualitatively explained from the difference of crystal radii of Ca^{2+} and Sr^{2+}, as shown by the broken line in Fig. 3. The U–O_I length of $CaUO_4$ is reasonable for the uranyl group, while that of α-$SrUO_4$ is larger.

2. *Lattice Parameter Change of $MeUO_{4-x}$ with Nonstoichiometry*

Figures 4, 5, and 6 show the variation of lattice parameters of the rhombohedral cell as a function of $4-x$ in $CaUO_{4-x}$, α-$SrUO_{4-x}$, and $(Ca_{0.5}Sr_{0.5})UO_{4-x}$, respectively. For $CaUO_{4-x}$ (Fig. 4), the products were two-phase mixtures in the $4-x$ range from 3.98 to 3.70. The two phases consist of the same $CaUO_{4-x}$ type crystals but differ in lattice parameters. The above result indicates that there are two homogeneity regions, $4.00 \sim 3.98$ and $3.70 \sim 3.50$. Below $4 - x = 3.70$, a(rhomb) increases linearly with decreasing $4-x$ with a rate da(rhomb)/$d(4 - x) = -0.36$ Å, while α(rhomb) decreases with a rate $d\alpha$(rhomb)/$d(4 - x) = 2.4°$. This result is not consistent with that of Holc and Kolar (*7*), who have reported that Guinier X-ray powder diffraction showed no line shifting for samples of $CaUO_{4-x}$ with the $4-x$ values from 4 to 3.57. They prepared the oxygen-deficient samples

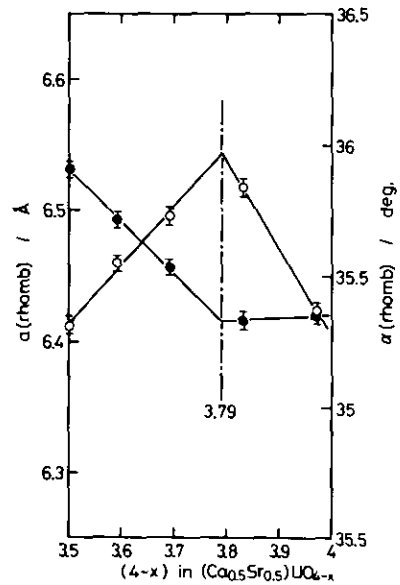

FIG. 6. Lattice parameters as a function of $4 - x$ in $(Ca_{0.5}Sr_{0.5})UO_{4-x}$: (●) a(rhomb); (○) α(rhomb).

by reducing $CaUO_4$ in a stream of hydrogen at 573 ~ 1173 K, but their samples were possibly oxidized before or during the X-ray diffraction analyses, which were performed in air. As we confirmed, the oxygen-deficient $CaUO_{4-x}$ is readily oxidized in air even at room temperature. The above disagreement, therefore, seems to be caused by oxidation of the samples.

For α-$SrUO_{4-x}$ (Fig. 5), on the other hand, the products were all single phase between $4 - x = 4.00$ and 3.50. The lattice parameter a(rhomb) remains unchanged in the region between $4 - x = 4.00$ and 3.77, whereas the rhombohedral angle α(rhomb) increases with $d\alpha(\text{rhomb})/d(4 - x) = -3.3°$ as $4 - x$ decreases in the same region. In the range below $4 - x = 3.77$, $da(\text{rhomb})/d(4 - x) = -0.24$ Å and $d\alpha(\text{rhomb})/d(4 - x) = 1.5°$, in sharp contrast to those in the former region.

The behavior of $(Ca_{0.5}Sr_{0.5})UO_{4-x}$ shown in Fig. 6 is similar to that of α-$SrUO_{4-x}$. Its lattice parameter a(rhomb) is nearly constant, while the angle α(rhomb) changes steeply with slope $d\alpha(\text{rhomb})/d(4 - x) = -3.4°$ between $4 - x = 4.00$ and 3.79. The $4 - x$ value which corresponds to the discontinuity point of the derivative, 3.79, is close to the value 3.77 for α-$SrUO_{4-x}$. In the region from $4 - x = 3.79$ to 3.50, a(rhomb) increases with decreasing $4 - x$ with a rate $da(\text{rhomb})/d(4 - x) = -0.39$ Å and α(rhomb) decreases with a rate $d\alpha(\text{rhomb})/d(4 - x) = 2.2°$. That is to say, the lattice parameter change of $(Ca_{0.5}Sr_{0.5})UO_{4-x}$ in the range $4 - x = 4.00 \sim 3.79$ is the same as that of α-$SrUO_{4-x}$ in the corresponding range of nonstoichiometry, and the change of $(Ca_{0.5}Sr_{0.5})UO_{4-x}$ in the range $4 - x = 3.79 \sim 3.50$ is the same as that of $CaUO_{4-x}$ for $4 - x = 3.70 \sim 3.50$ as judged from the values of the slopes.

Figure 7 shows the variation of the rhombohedral cell volume as a function of $4 - x$ in $MeUO_{4-x}$. For α-$SrUO_{4-x}$ and $(Ca_{0.5}Sr_{0.5})UO_{4-x}$, slope changes appear in the curves at the $4 - x$ values corresponding to the slope changes in the lattice parameters. The volume change is more rapid in the region of the small oxygen deficiencies.

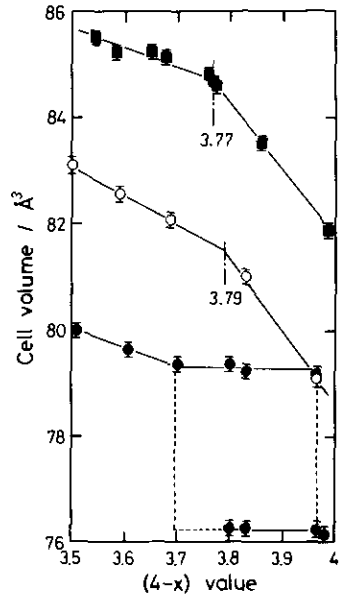

FIG. 7. Rhombohedral cell volume as a function of $4 - x$ value: (●) $CaUO_4$; (■) α-$SrUO_4$; (○) $(Ca_{0.5}Sr_{0.5})UO_4$.

3. *Atomic Parameter Change of α-$SrUO_{4-x}$ with Nonstoichiometry*

The occupation factor of oxygen on the O_I and O_{II} sites was obtained for α-$SrUO_{4-x}$ as the one which yields the best fit of the calculated X-ray diffraction intensities with the observed intensities, i.e., the minimum R-value. Calculation was carried out for $4 - x = 3.777$ and 3.597 samples. The occupation factor, z, can be represented for each of these samples as α-$SrUO_{I_z}O_{II_{3.777-z}}$ and α-$SrUO_{I_z}O_{II_{3.597-z}}$. The minimized R-value with respect to the u and v parameters was calculated for each z value. The change of this R-value with z is shown in Fig. 8. It is seen from the figure that the R-value decreases steadily with increasing z up to $z = 2$ for both α-$SrUO_{3.777}$ and α-$SrUO_{3.597}$. This result shows that the oxygen vacancies are formed only on the O_{II} sites, and not on the O_I sites in nonstoichiometric α-$SrUO_{4-x}$.

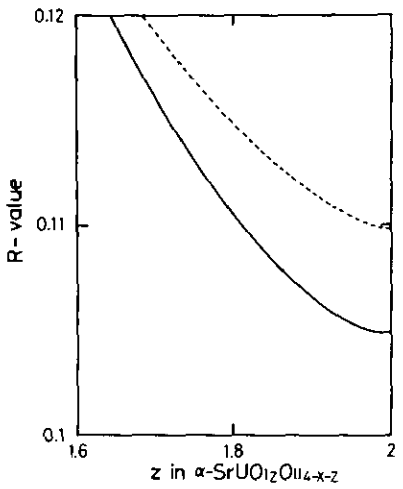

FIG. 8. Variation of R-value as a function of z in α-$SrUO_{I_z}O_{II_{4-x-z}}$: (—) α-$SrUO_{I_z}O_{II_{3.777-z}}$; (– – –) α-$SrUO_{I_z}O_{II_{3.597-z}}$.

The same may also be true for $CaUO_{4-x}$ and $(Ca_{0.5}Sr_{0.5})UO_{4-x}$.

The atomic parameters of oxygen, u and v, were determined for highly nonstoichiometric α-$SrUO_{4-x}$ ($4 - x = 3.777$ and 3.597) as well as for nearly stoichiometric α-$SrUO_{3.978}$ in order to learn the effect of nonstoichiometry on interatomic distances. The result is listed in Table II together with lattice parameters, cell volumes, etc. Some of the interatomic distances are depicted in Fig. 9 as a function of $4 - x$. This shows that the U–O_{II} distance remains unchanged between $4 - x = 3.978$ and 3.597. The distance is close to the sum of the crystal radii of the weighed average of U^{6+} and U^{5+} and O^{2-} (*24*). The line of the Sr–O_{II} separation is horizontal above $4 - x = 3.777$, the separation being very close to the crystal radius sum, while below 3.777 the discrepancy increases. On the other hand, the Sr–O_I distance comes near to the crystal radius sum of Sr^{2+} and O^{2-} below $4 - x = 3.777$.

4. *General Features of the Crystal Structure*

The strongest bonds in the crystals of $Ca_{1-y}Sr_yUO_{4-x}$ ($y = 0$, 0.5, and 1) are formed between uranium and oxygen, since uranium has the highest valence in the compounds. Thus, it is reasonable to consider that the U–O bonds play the main role in construction of the skeleton of the crystal and that the *Me*–O bonds work to modify the lattice parameters and atomic parameters first defined by the U–O bonds.

The U–O_{II} bond length does not change with y in $Ca_{1-y}Sr_yUO_4$ (Fig. 3) or with nonstoichiometry (Fig. 9). As seen from Table I, a(rhomb) increases nearly linearly with increasing y of $Ca_{1-y}Sr_yUO_4$, which can be understood as due to the larger crystal radius of Sr^{2+}. This increase requires a decrease of α(rhomb) to keep the U–O_{II} distance unchanged. In fact, α(rhomb) decreases from 36.04° for $CaUO_{3.981}$ to 34.83° for α-$SrUO_{3.978}$ (Table I). This is to say, as the crystal radius of Me^{2+} increases, the rhombohedral cell shown in Fig. 2 becomes taller and thinner. It should be noted that the cell volume is still increased as shown in Fig. 7.

The length of the vertical bonds *Me*–O_{II}, on the other hand, is seen to change with y in such a manner that the length is essentially the sum of the crystal radii of Me^{2+}

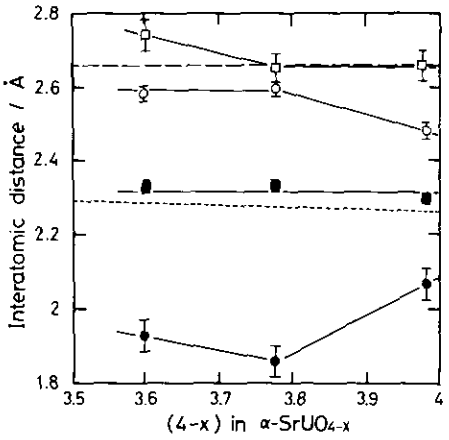

FIG. 9. Interatomic distances as a function of $4 - x$ in α-$SrUO_{4-x}$: (●) U–O_I; (■) U–O_{II}; (○) Sr–O_I; (□) Sr–O_{II}; (---) sum of crystal radii of weighted average of U^{6+}, U^{5+}, and O^{2-} (*24*); (– – –) sum of crystal radii of Sr^{2+} and O^{2-} (*24*).

and O^{2-} (Fig. 3). This change is considered to be made possible because the Me–O_{II} bond is close to normal to the U–O_{II} bond, and therefore its change affects the U–O_{II} distance only with the second order.

The atomic parameter u defines the O_I position in combination with the lattice parameters. The U–O_I bonds compose the uranyl group which is the shortest and strongest in this compound. This bond length increases as y increases, and it reaches as long as 2.07 Å for α-$SrUO_{3.978}$. By contraries, the Me–O_I distance does not change with y (Fig. 3). If one takes into account the crystal radius change of Me^{2+}, however, this fact is rather unnatural. The observed Sr–O_I distance of 2.48 Å is significantly shorter than the crystal radius sum of 2.66 Å (*24*). If the Sr–O_I distance was longer, the U–O_I distance would have been shortened (Fig. 2). This fact can be regarded to cause destabilization of the α-$SrUO_4$ crystal.

It is important that the effect of oxygen nonstoichiometry is different in two $4 - x$ regions. For α-$SrUO_{4-x}$ (Fig. 5) and $(Ca_{0.5}Sr_{0.5})UO_{4-x}$ (Fig. 6), although α(rhomb) steeply increases as $4 - x$ decreases, a(rhomb) remains almost constant. This type of lattice parameter change leads to a significant decrease in U–O_I distance with decreasing $4 - x$ value (Fig. 9). As a result, the U–O_I distance of α-$SrUO_{3.777}$ is decreased to 1.86 Å, which is short enough for a uranyl bond which is usually in the range of 1.7 ~ 1.9 Å. Thus, the $4 - x$ dependence of the lattice parameter has to change below $4 - x = 3.777$, since otherwise the distance becomes too short. The lattice parameter a(rhomb) increases with decreasing $4 - x$ in the range from $4 - x = 3.77$ to 3.50, while α(rhomb) decreases in the same range as seen in Fig. 5, which causes a small increase in the U–O_I distance of α-$SrUO_{4-x}$ and in the u value (Table II). This increase below $4 - x = 3.77$ is reasonable because of the increase in the mean radius of uranium as the uranium valence decreases with decreasing $4 - x$ value. Another point to be described here is that a smaller separation of the O_{II} plane from the uranium plane is observed for α-$SrUO_{4-x}$ as $4 - x$ decreases from 3.777 to 3.597 (Table II). When more oxygen atoms are taken out from the O_{II} sites of the crystal, the O_{II} planes above and below the uranium atom come closer due to reduction in electrostatic repulsion, leading to an increase in the Sr–O_{II} distance. It is noteworthy that the slopes of the lattice parameter change are basically the same for $CaUO_{4-x}$ and $(Ca_{0.5}Sr_{0.5})UO_{4-x}$ but different from those of α-$SrUO_{4-x}$ in the low $4 - x$ region. The reason for this difference is unclear. Efforts to collect X-ray intensity information on highly reduced $CaUO_{4-x}$ and $(Ca_{0.5}Sr_{0.5})UO_{4-x}$ with a diffractometer were unsuccessful because the specimens were extremely susceptible to oxidation. One explanation is that the steeper slope becomes possible for $CaUO_{4-x}$ and $(Ca_{0.5}Sr_{0.5})UO_{4-x}$ due to smaller a(rhomb). It is characteristic for $CaUO_{4-x}$ that the lattice parameters misfit at $4 - x = 3.70$, producing a two phase mixture above this nonstoichiometry up to nearly 4.

5. *Enthalpy of Formation of α-$SrUO_{4-x}$*

The thermochemical cycle from which $\Delta_f H^\circ$ (α-$SrUO_{4-x}$, c) was calculated is shown in Table III. The heats of solution of α-$SrUO_{4-x}$ in 5.94 M HCl are given in Table IV. Table V shows the resultant values of $\Delta_f H^\circ$ (α-$SrUO_{4-x}$, c). We note that our value of $\Delta_f H^\circ$ (α-$SrUO_4$, c), -1989.1 ± 2.9 kJ · mol^{-1}, agrees well with the literature value, -1985.3 ± 2.1 kJ · mol^{-1} (*29*), within stated uncertainty limits. This literature value is that which was obtained by correcting the value of Ref. (*6*) with more recent values of auxiliary data.

According to O'Hare *et al.* (*12*), the enthalpy of formation of stoichiometric $CaUO_4$ is -2002 ± 2 kJ · mol^{-1} at 298 K. This $\Delta_f H^\circ$ value is lower than that of α-$SrUO_4$ by 13 kJ · mol^{-1}. It should be noted, however, that the enthalpies of formation of $MeUO_4$ (Me = Mg, Ca, Sr, and Ba) from

TABLE III

THERMOCHEMICAL CYCLE FOR $\Delta_f H°$ (α-$SrUO_{4-x}$, c)/kJ · mol^{-1} IN 5.94 mol · dm^{-3} HCl

(1) α-$SrUO_{4-x}$(c) + 2(2 + x)HCl(5.94 mol · dm^{-3} HCl) = [$SrCl_2$ + $xUCl_4$ + (1 − x)UO_2Cl_2 + (2 + x)H_2O] (in 5.94 mol · dm^{-3} HCl)
ΔH_1

(2) (1 − x)UO_2Cl_2(c) = (1 − x)UO_2Cl_2 (in 5.94 mol · dm^{-3} HCl)
$\Delta H_2 = (-64.0 \pm 2.0)(1 - x)$ (25)

(3) $SrCl_2$(c) = $SrCl_2$ (in 5.94 mol · dm^{-3} HCl)
$\Delta H_3 = -31.8 \pm 1.0$ (19, 26)

(4) (1 − x)U(c) + (1 − x)O_2(g) + (1 − x)Cl_2(g) = (1 − x)UO_2Cl_2(c)
$\Delta H_4 = (-1243.9 \pm 1.3)(1 - x)$ (25, 27)

(5) Sr(c) + Cl_2(g) = $SrCl_2$(c)
$\Delta H_5 = -833.7 \pm 1.0$ (19)

(6) 2(2 + x)HCl(5.94 mol · dm^{-3} HCl) = (2 + x)H_2(g) + (2 + x)Cl_2(g)
$\Delta H_6 = (153.7 \pm 0.1) \cdot 2(2 + x)$ (28)

(7) (2 + x)H_2(g) + (2 + x)O_2(g) = (2 + x)H_2O (in 5.94 mol · dm^{-3} HCl)
$\Delta H_7 = (-286.70 \pm 0.04)(2 + x)$ (28)

(8) $xUCl_4$(c) = $xUCl_4$ (in 5.94 mol · dm^{-3} HCl)
$\Delta H_8 = (-166.3 \pm 4.0)x$ (25)

(9) xU(c) + 2$x$$Cl_2$(g) = $xUCl_4$(c)
$\Delta H_9 = (-1019.2 \pm 2.5)x$ (25, 27)

$\Delta_f H°$ (α-$SrUO_{4-x}$, c) = $-\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 + \Delta H_8 + \Delta H_9$

TABLE IV

CALORIMETRIC RESULTS FOR THE REACTION OF α-$SrUO_{4-x}$ WITH HCl

4 − x	m(α-$SrUO_{4-x}$)/g	ΔH/J	ΔH_{sol}/kJ · mol^{-1}
3.522	0.11177	−50.055	−171.074
	0.12620	−56.052	−169.666
	0.12190	−54.541	−170.916
	Average:		−170.55 ± 0.63
3.620	0.11719	−46.616	−152.574
	0.10616	−42.341	−152.982
	0.11895	−47.316	−152.575
	Average:		−152.71 ± 0.19
3.703	0.10276	−39.968	−149.704
	0.12719	−49.248	−149.033
	0.14730	−57.016	−148.984
	Average:		−149.24 ± 0.33
3.873	0.09812	−35.603	−140.644
	0.10439	−38.399	−142.578
	0.10628	−40.264	−146.844
	Average:		−143.4 ± 2.6
4.000	0.07889	−28.697	−141.737
	0.09710	−35.697	−143.246
	0.09049	−33.352	−143.613
	Average:		−142.86 ± 0.81

binary oxides become more negative in the sequence Mg–Ba (*30*).

The $\Delta_f H°$ values of table V for nonstoichiometric α-$SrUO_{4-x}$ are plotted as a function of 4 − x in Fig. 10. The $\Delta_f H°$ value monotonously increases with decreasing 4 − x in α-$SrUO_{4-x}$, with an increment which becomes larger as 4 − x decreases. Least-squares calculation was performed by assuming that its change can be expressed by a second-order polynomial. The result is

$$\Delta_f H°(\alpha\text{-}SrUO_{4-x}, c)/\text{kJ} \cdot \text{mol}^{-1} = -1989.1 + 100.3x + 188.5x^2. \quad (2)$$

TABLE V

STANDARD ENTHALPIES OF FORMATION OF α-$SrUO_{4-x}$ AT 298.15 K

(4 − x) of $SrUO_{4-x}$	ΔH_1/kJ · mol^{-1}	$\Delta_f H°$ (α-$SrUO_{4-x}$, c)/kJ · mol^{-1}
3.522	−170.55 ± 0.63	−1893.0 ± 3.0
3.620	−152.71 ± 0.19	−1924.9 ± 2.8
3.703	−149.24 ± 0.33	−1940.3 ± 2.7
3.873	−143.4 ± 2.6	−1970.5 ± 3.7
4.000	−142.86 ± 0.81	−1989.1 ± 2.9

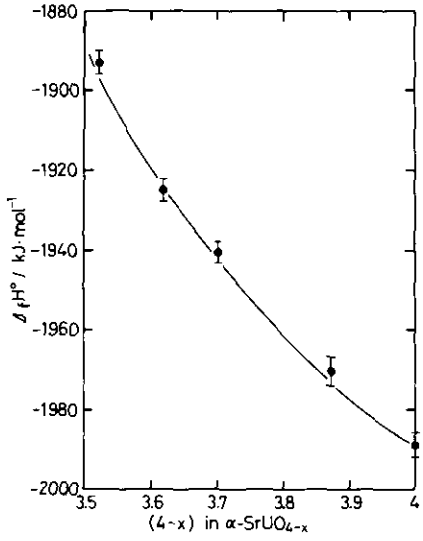

FIG. 10. Enthalpy of formation as a function of $4 - x$ in α-$SrUO_{4-x}$: (●) observed; (—) calculated by Eq. (2).

The solid line in Fig. 10 shows the $\Delta_f H^\circ$ change by this equation, which is seen to follow satisfactorily the observed points.

The positive second-order term of x in Eq. (2) indicates the existence of repulsive vacancy–vacancy interactions in oxygen-deficient α-$SrUO_{4-x}$. The upward concave curve in Fig. 10 is similar to that found for $\Delta_f H^\circ$ of $BaUO_{3+x}$ (*30*).

6. *Partial Molar Enthalpy of Oxygen in α-$SrUO_{4-x}$*

The partial molar enthalpy of oxygen, $\Delta\overline{H}_{O_2}$, can be calculated by differentiating the integral enthalpy of formation with respect to x as

$$\Delta\overline{H}_{O_2} = -2\frac{d[\Delta_f H^\circ(\alpha\text{-}SrUO_{4-x}, c)]}{dx}. \quad (3)$$

From Eqs. (2) and (3) we have

$$\Delta\overline{H}_{O_2}/\text{kJ}\cdot\text{mol}^{-1} = -200.6 - 753.9x, \quad (4)$$

for which the x dependence is depicted in Fig. 11 as the solid line. The broken line near $4 - x = 3.5$ shows the estimated $\Delta\overline{H}_{O_2}$ change. The curve rapidly decreases as the $4 - x$ value approaches to 3.5 corresponding to the sharp supposed decline of $\Delta\overline{G}_{O_2}$ as the $4 - x$ decreases to a lower phase limit.

Since two moles of O_2 react with each one mole of strontium and uranium atoms to form one mole of stoichiometric α-$SrUO_4$, the following relation holds at $x = 0$:

$$[\Delta_f H^\circ(\alpha\text{-}SrUO_{4-x}, c)]_{x=0} = 2[\Delta\overline{H}_{O_2}]_{x=0}. \quad (5)$$

This equation leads to $[\Delta\overline{H}_{O_2}]_{x=0} = -994.6 \pm 1.5\ \text{kJ}\cdot\text{mol}^{-1}$. Such a low value cannot be connected directly with the partial molar enthalpies given by Eq. (4), but here we recall the observation by Picard and Gerdanian (*31*) for $\Delta\overline{H}_{O_2}$ of UO_{2+x} near $x = 0$. They measured the partial molar enthalpy of oxygen using a Tian–Calvet type microcalorimeter and found that $\Delta\overline{H}_{O_2}$ first rapidly increases and then very sharply decreases as the x value decreases toward zero. The broken line near $4 - x = 4.0$ of Fig. 11 shows the outline of the $\Delta\overline{H}_{O_2}$ change for α-$SrUO_{4-x}$ as obtained by assuming a similar

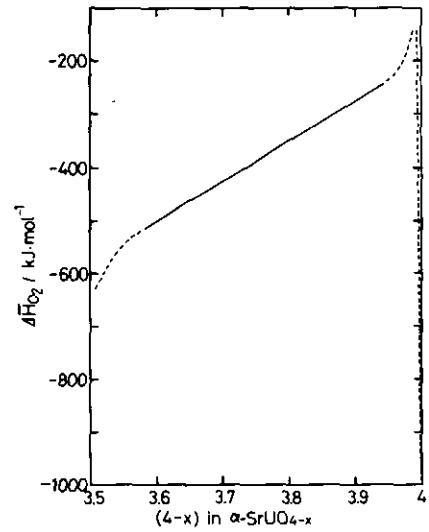

FIG. 11. Partial molar enthalpy of oxygen, $\Delta\overline{H}_{O_2}$, for α-$SrUO_{4-x}$ calculated by using Eq. (4).

trend to UO_{2+x} in the vicinity of the stoichiometry. It is seen that $[\Delta\overline{H}_{O_2}]_{x=0}$ can basically be connected with Eq. (5) if the curve of $\Delta\overline{H}_{O_2}$ has correctly the shape of Fig. 11. This type of maximum in $\Delta\overline{H}_{O_2}$ is considered to suggest that there exists a competitive reaction of formation of two kinds of defects or defect complexes. In the case of UO_{2+x}, the sharp maximum of $\Delta\overline{H}_{O_2}$ at $x = 0.002$ has been explained by the formation of oxygen intertials or Willis clusters containing oxygen interstitials in combination with oxygen vacancies (*32, 33*). For the present compounds also, some interaction between oxygen vacancies and interstitials having formation energies of different x dependencies could be assumed. But for detailed discussion more thermochemical data are required.

Due to difficulty in dissolution of $CaUO_{4-x}$ in hydrochloric acid, we did not measure $\Delta_f H°$ ($CaUO_{4-x}$, *c*) for this compound. Anderson and Barraclough (*34*) have measured the equilibrium oxygen pressure over $CaUO_{4-x}$ in the temperature range 900 ~ 1250 K and calculated the partial molar enthalpy of oxygen of this material. On the other hand, Jakeš (*35*) measured the EMF of solid state cells containing *Me*U O_{4-x}(*Me* = Mg, Ca, Sr, and Ba) in the temperature range from around 1050 to 1333 K and calculated the partial molar enthalpy of oxygen for these oxides. Our measurements were made at 298 K and thus the measured values cannot be directly compared with those at high temperatures, but if corrected for standard states, Anderson and Barraclough's $\Delta\overline{H}_{O_2}$ in $CaUO_{4-x}$ has quantitatively the same dependence upon x, although a much larger magnitude, as does ours in α-$SrUO_{4-x}$. The result of Jakeš for $CaUO_{4-x}$, however, is much smaller than that of Anderson and Barraclough and his value for α-$SrUO_{4-x}$, $\Delta\overline{H}_{O_2} = -28.8$ kJ · mol^{-1}, is much smaller than ours. This may be because EMF measurements tend to give $\Delta\overline{G}_{O_2}$ values having larger uncertainties at higher $4 - x$.

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