

## Phase Relations and Crystal Chemistry of Solid Solution, $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$

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Solid solutions,  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$ , were prepared by heating the mixtures of  $\beta\text{-SrUO}_4$ ,  $\text{UO}_2$ , and  $\text{U}_3\text{O}_8$  in either helium or vacuum. When heated in helium at 1300 or 1400°C, a single-phase cubic fluorite (face centered cubic, FCC) phase was obtained up to strontium concentration ( $y$  of  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$ ) ca. 0.3, although it splits into two fluorite phases around  $y = 0.03, 0.05,$  and  $0.08$  during the relatively slow cooling process. Due to larger  $x$  values of  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$ , for the samples heated at 1200°C, a single rhombohedral phase was formed in the range  $0.06 \leq y \leq 0.10$ . The  $x$  value and uranium valency in the solids showed steep change at  $y = 0.03, 0.06,$  and  $0.09$ , which is presumably related to the stepwise ordering of strontium atoms to form the rhombohedral phase. A statistical thermodynamical calculation was made concerning this transition. When heated in vacuum, only the FCC phase was formed below  $y = 0.15$ . For this phase, the lattice parameter change was expressed as linear functions of  $x$  and  $y$  by least-squares fittings. The coefficient of  $y$  of these equations was found to be on a straight line irrespective of the valency of the foreign cation if the net change in crystal radius was taken as the variable. © 1988 Academic Press, Inc.

### Introduction

Solid solutions,  $\text{M}_y\text{U}_{1-y}\text{O}_{2+x}$ , where the  $M$  metal atoms substitute for the U are known to form comparatively easily under certain reaction conditions. Tetravalent  $M$  ions such as  $\text{Th}^{4+}$  (1),  $\text{Zr}^{4+}$  (2), and  $\text{Ce}^{4+}$  (3) would be the most natural substituents since uranium occurs as  $\text{U}^{4+}$  in  $\text{UO}_2$ , but trivalent lanthanide elements and some of the divalent alkaline earth metals also form solid solutions. If these contain foreign metal atoms with formal valency less than four, valence compensation is attained

through the oxidation of uranium in the crystal unless a corresponding amount of oxygen is removed. The degree of oxygen nonstoichiometry is a function of oxygen partial pressure and temperature. Crystal chemical study of these solid solutions in relation with the valence change and oxygen nonstoichiometry is important for discussion of the irradiation behavior of nuclear fuels.

In our former studies on the solid solutions containing alkaline earth metals, i.e.,  $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$  (4, 5) and  $\text{Ca}_y\text{U}_{1-y}\text{O}_{2+x}$  (6), the cubic fluorite-type phases were found to

extend up to  $y = 0.33$  on heating in helium to  $1200^\circ\text{C}$ . In these solid solutions, the foreign atoms statistically occupy the uranium atom sites, and the excess oxygen atoms expressed by  $x$  are in the interstitial position of the  $\text{UO}_2$  lattice.

Electromotive force measurements of  $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$  at temperatures between  $700$  and  $1050^\circ\text{C}$  (7, 8) revealed that the partial molar free energy of oxygen,  $\Delta\bar{G}_{\text{O}_2}$ , increases largely with incorporation of the magnesium ion and that the observed dependence of partial molar entropy of oxygen,  $\Delta\bar{S}_{\text{O}_2}$ , on  $y$  of  $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$  could well be described by the equation derived from a statistical model which assumes random distribution of  $\text{U}^{5+}$  ions formed by the introduction of magnesium as well as by the excess oxygen ions.

Strontium is produced in the fuel during burn-up with considerably high fission yield. However, the phase behavior of its solid solution,  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$ , which could be a homolog of the magnesium and calcium solid solutions has not yet been well elucidated. McIver (9) heated the mixture of  $\text{SrO}$  and  $\text{UO}_2$  in various ratios under an oxygen potential of  $-110 \text{ kcal}_{\text{th}} \cdot \text{mole}^{-1}$  at  $1500^\circ\text{C}$  and found that the maximum solubility of  $\text{SrO}$  was 12 mole%. The lattice parameter of the cubic solid solution was specified by a linear equation,  $a = 5.4700 - 0.0046t$ , where  $t$  represents the  $\text{SrO}$  mole percentage in  $\text{UO}_2$ . Nevertheless, the important properties of this system, namely the oxygen stoichiometry in the solid solution and phase stability with respect to temperature and oxygen partial pressure remain unresolved.

This paper describes work on  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$  prepared by heating the mixtures of  $\text{SrUO}_4$ ,  $\text{U}_3\text{O}_8$ , and  $\text{UO}_2$  either in helium or in vacuum at temperatures from  $1100$  to  $1500^\circ\text{C}$  with the intention of clarifying the above points. Single-phase regions of the solid solutions were studied by X-ray diffraction techniques. The lattice parameter

change in this region was expressed as a linear function of  $x$  and  $y$  of  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$ . From the anomalies in the curves of  $x$  vs  $y$  and lattice parameter vs  $y$ , the ordering of strontium and uranium is believed to occur in the solid solution under conditions associated with formation of rhombohedral phase. This phase transformation will be discussed as related to the  $x$  and  $y$  values.

## Experimental

### 1. Materials Used

Strontium carbonate was precipitated from strontium nitrate solution by the addition of ammonium carbonate. The precipitate was filtered out, washed with water, and dried at  $200^\circ\text{C}$ .

Triuranium octoxide,  $\text{U}_3\text{O}_8$ , was prepared by air oxidation of high-purity uranium metal at  $700^\circ\text{C}$  (10).

Uranium dioxide was prepared by reducing  $\text{U}_3\text{O}_8$  in a stream of hydrogen at  $1000^\circ\text{C}$  for 10 hr.

Strontium monouranate,  $\beta\text{-SrUO}_4$ , was prepared by heating the intimate mixture of  $\text{SrCO}_3$  and  $\text{UO}_2$  (1:1) in air at  $900^\circ\text{C}$ . The mixing and heating cycle was repeated thrice in order to obtain a homogeneous product. The X-ray powder diffraction pattern agreed well with that reported for  $\beta\text{-SrUO}_4$  (11).

### 2. Reaction Procedure

Calculated amounts of  $\text{SrUO}_4$ ,  $\text{U}_3\text{O}_8$ , and  $\text{UO}_2$  were weighed to have the bulk compositions  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2.10}$  and intimately mixed in an agate mortar for roughly 1 hr. To obtain homogeneous products, mixing was performed by diluting successively the mixture of higher  $y$  value with  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$ ; e.g., the  $y = 0.08$  mixture was obtained by mixing the  $y = 0.1$  mixture with calculated amounts of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  and the  $y = 0.07$  mixture by mixing the  $0.08$  mixture with  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  and so on. The  $y$  value of the

mixtures ranged from 0.005 to 0.4; they were pressed into pellets of 7 mm diameter, each having the weight 0.6–0.8 g. A series of experiments was carried out by heating the pellets of various  $y$  values on a platinum sheet in helium purified with hot (500°C) copper tube. The oxygen pressure in the helium was determined to be  $6.3 \times 10^{-3}$  Torr  $O_2$  from the resistance of nonstoichiometric cobalt oxide wire at 1000°C (12). The flow rate of the gas was  $6 \text{ ml} \cdot \text{min}^{-1}$ . After reaction, the furnace was cooled on standing.

Another series of experiments was carried out by heating the mixture pellets in a high-vacuum furnace with  $1 \times 10^{-6}$  Torr  $O_2$ . The cooling rate was basically the same as in the helium case. Black sintered pellets were obtained by either of the reactions.

### 3. X-ray Measurements

The X-ray powder photographs were taken for powder samples in glass capillaries with a Norelco 114.6-mm camera using the nickel-filtered  $\text{CuK}\alpha$  radiation. The diffractometer experiments were carried out with a Philips PW-1390 using  $\text{CuK}\alpha$  radiation monochromatized with a bent pyrolytic graphite monochromator placed between specimen and  $\text{NaI(Tl)}$  detector. The slit system used was  $\frac{1}{2}^\circ$ –0.1 mm– $\frac{1}{2}^\circ$ . The estimated error in lattice parameters is  $\pm 0.0005 \text{ \AA}$  for well-crystallized cubic single-phase specimens, whereas it becomes sometimes as large as  $\pm 0.002 \text{ \AA}$  for poorly-crystallized crystals and/or two-phase mixtures.

### 4. Chemical Analysis

The amounts of total uranium ( $U^{4+}$  and  $U^{6+}$ ) and  $U^{4+}$  were determined separately by cerimetric analysis (13, 14). The  $x$  and  $y$  values of  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$  can be calculated from these amounts in terms of the charge neutrality condition. If the vaporization of strontium and/or uranium during heating reaction is negligibly small, the  $y$  value of

the product coincides with that before heating. This was found to hold by the separate determinations above. Thereafter, the oxygen amount was determined solely by  $U^{4+}$  titration. The error in  $x$  values is estimated to be less than  $\pm 0.003$ .

## Results and Discussion

### 1. Reaction in Helium

The X-ray diffraction pattern of the products obtained by heating the mixtures in helium for 50 hr showed that the crystal was face centered cubic (FCC) for certain ranges of strontium concentration. Figure 1 indicates the variation of lattice parameter of the FCC phase for strontium concentrations  $y \geq 0.1$  and delineates both single- and multiphase regions of cubic strontium solid solution,  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$ . For  $y = 0.4$  samples, many concomitant diffraction lines from another noncubic crystal structure

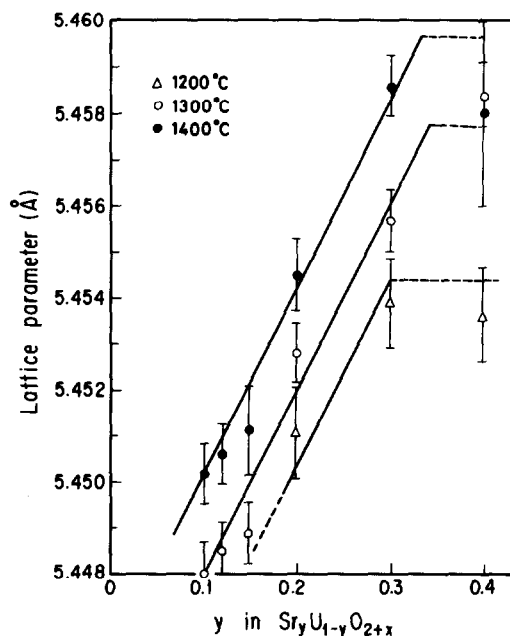


FIG. 1. Lattice parameter of the specimens heated in He as a function of  $y$  at high strontium concentrations.  $\Delta$ , 1200°C;  $\circ$ , 1300°C;  $\bullet$ , 1400°C.

were encountered, deriving possibly from some strontium uranate having a Sr/U ratio  $\geq \frac{1}{2}$ . The upper limit of the single-phase region of cubic solid solution is roughly  $y = 0.3$  at temperatures 1200–1400°C, close to those of  $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$  (4) and  $\text{Ca}_y\text{U}_{1-y}\text{O}_{2+x}$  (6), viz.,  $y = 0.33$ , when heated in helium. In both the magnesium and calcium compounds, the FCC phase was formed for all  $y$  in the range  $0 \leq y \leq 0.33$ . However, the  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$  precipitates as a rhombohedral phase between  $y = 0.06$  and 0.1; its complex phase relation will be described later.

The lattice parameter of the cubic phase  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$  changes with both  $y$  and  $x$ ; the latter value is contained implicitly in the parameters of Fig. 1. The function which relates the lattice parameter with  $y$  and  $x$  will be discussed under Section 2.

The reaction rate was lower for smaller  $y$ . The samples where  $y < 0.15$  were heated for 50 hr at their respective temperatures, finely ground, pressed into pellets, and reheated three times under the same reaction condition. Figure 2 shows the relation between  $y$  and  $x$  values for the specimens thus obtained. Generally,  $x$  decreases with increasing  $y$ , although sharp changes in  $x$  occur near  $y = 0.03, 0.06,$  and  $0.09$  for each of the samples heated at 1200, 1300, and 1400°C. The  $x$  values larger than the bulk compositions  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2.10}$  before heating are considered to arise from oxygen pick-up from the helium gas during the long heating period of 150 hr.

These samples may not be in strict thermodynamic equilibrium with the oxygen in helium: near the solid surface the oxygen pressure may differ from the bulk if oxygen is absorbed or desorbed. A longer period may be required for diffusion and because of the much smaller area of the flat surface of the pellets compared with powder. Despite these factors, it is likely that the curves in Fig. 2 express nearly equilibrium isobars. The relation between  $y$  and  $x$  may be derived by a statistical model (15). When  $\text{U}^{4+}$  is oxidized to  $\text{U}^{5+}$  by introduction of

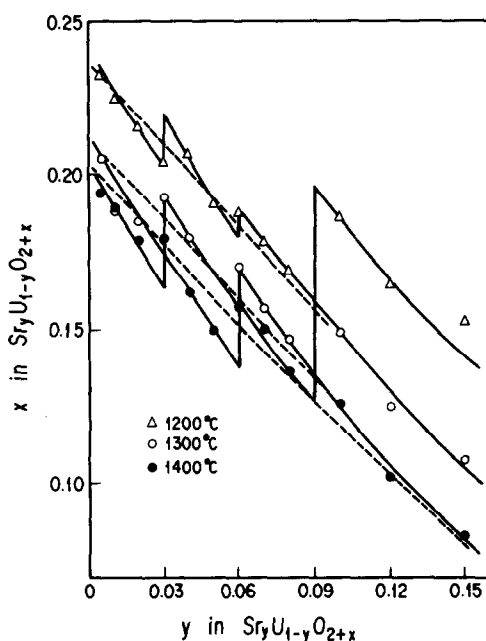


FIG. 2. Variation of  $x$  value in  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$  with  $y$  for the samples heated in He.  $\Delta$ , 1200°C;  $\circ$ , 1300°C;  $\bullet$ , 1400°C. Errors in  $x$  are estimated to be  $\pm 0.003$ . Broken lines show theoretical values.

$\text{Sr}^{2+}$  as well as excess  $\text{O}^{2-}$ , one obtains the partial molar entropy of oxygen,  $\Delta\bar{S}_{\text{O}_2}$  by differentiating the number of arrangements of these cations with respect to  $x$ , as in the case of  $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$  (4). This yields

$$\Delta\bar{S}_{\text{O}_2} = -2R \cdot \ln \frac{x}{1-x} - 4R \cdot \ln \frac{2x-2y}{1-2x-3y} + Q, \quad (1)$$

where  $Q$  includes the vibrational term which does not vary greatly with the composition of the solid solution. If the partial molar enthalpy of oxygen  $\Delta\bar{H}_{\text{O}_2}$  is assumed not to change with  $x$  and  $y$ , as is likely for  $\text{UO}_{2+x}$  in  $0.05 \leq x \leq 0.20$  (16), the following equation holds.

$$\ln \left( \sqrt{\frac{x}{1-x}} \frac{2x-2y}{1-2x-3y} \right) = \frac{1}{4R} (R \cdot \ln p_{\text{O}_2} + Q - \frac{\Delta\bar{H}_{\text{O}_2}}{T}) = C, \quad (2)$$

where  $p_{O_2}$  is the equilibrium oxygen pressure and  $C$  is a constant at a given temperature.  $C$  values calculated from the  $x$  and  $y$  values of Fig. 2 yielded the averages  $C = -0.68 \pm 0.05$ ,  $-0.96 \pm 0.09$ , and  $-1.06 \pm 0.08$  for 1200, 1300, and 1400°C, respectively. Because the  $C$  values began to increase above  $y = 0.10$  for 1200 and 1300°C, these were excluded from the above calculation of the averages. The broken lines in Fig. 2 show the theoretical curve obtained by using the above  $C$  values. The relation between  $y$  and  $x$  is well reproduced by this model although the jumps cannot be simulated. Calculation of  $\Delta\bar{H}_{O_2}$  and/or  $Q$  could not be carried out under the prevailing experimental conditions.

The variation of mean valency of uranium, as calculated from the  $x$  values of Fig. 2, is shown in Fig. 3. For the moderate oxygen partial pressure in helium, the valency is still close to +4.4 even at  $y = 0$  and increases with  $y$  for all three curves. The

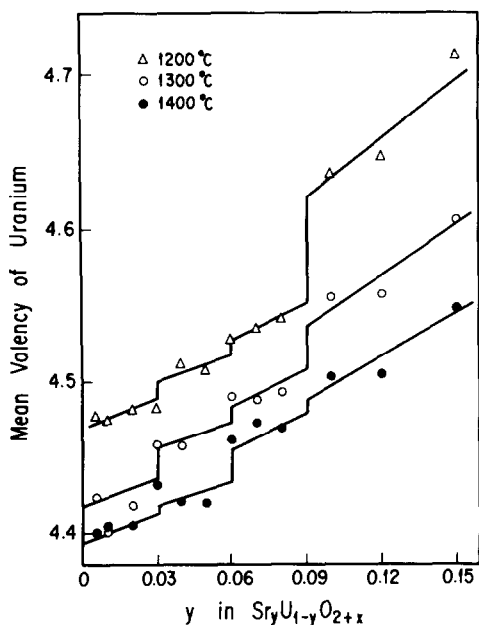


FIG. 3. Change of mean valency of uranium in the samples heated in He.  $\Delta$ , 1200°C;  $\circ$ , 1300°C;  $\bullet$ , 1400°C.

effect of strontium atoms on the valency of uranium is considered to be basically the same as for the lanthanides (17). The discontinuities at 0.03, 0.06, and 0.09 are, however, characteristic of this system.

The stability of  $Sr_yU_{1-y}O_{2+x}$  was checked by placing the powder in a silica gel desiccator. The samples ( $\sim 1$  g) did not change in mass within the  $\pm 20$   $\mu$ g error of microbalance on one month's standing in the desiccator: The solid solutions are stable against oxidation in air at room temperature.

The X-ray diffraction lines of the 1200°C samples were broad even after heating three times; they could be assigned to the FCC phase for lower  $y$ . However, the specimen with  $y = 0.05$  was a mixture of the FCC phase and a rhombohedral phase which develops to a single phase at  $y = 0.06$  and 0.07 with sharp diffraction lines. For  $y > 0.08$ , these lines broadened with increasing  $y$  and became very broad at  $y = 0.15$ , but sharp lines were again obtained for the FCC phase at  $y = 0.2$ . For the samples heated at 1300 and 1400°C, the rhombohedral phase did not appear because the  $x$  values are lower at higher temperatures. The existence range of the rhombohedral phase will be reported in a future paper (18) but the single-phase region occurs in the ranges  $0.06 \cong y \cong \text{ca. } 0.10$  and  $x \cong 0.17$ .

Samples heated at 1300 and 1400°C are face centered cubic but such specimens were sometimes two-phase mixtures, each being face centered cubic. They are designated as the 5.443- and 5.447-Å phases for simplicity although some excursion of lattice parameter occurs with composition. The relative intensity of the X-ray peaks for these phases is schematically drawn in Fig. 4, the solid and dashed lines representing the 5.447- and 5.443-Å phases, respectively. For the most part, the 5.447-Å phase is encountered except for  $y = 0.005$ , where the 5.443-Å phase is dominant. The 5.443-Å phase reappears at  $y = 0.03$ , though in small amounts (about  $\frac{1}{4}$  of the 5.447-Å

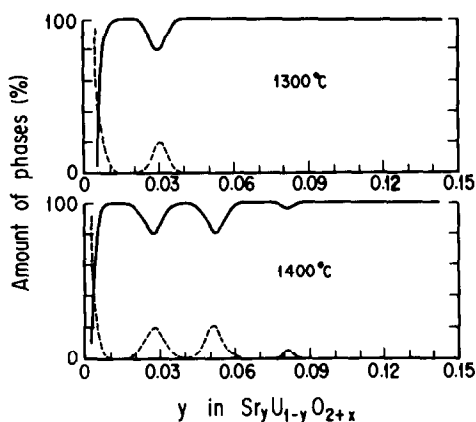


FIG. 4. Existence and estimated amounts of phases which vary with  $y$  at low strontium concentrations for samples heated in He. Solid line, 5.447-Å phase; dashed line, 5.443-Å phase.

phase). For 1400°C samples, the 5.443-Å phase appears also near  $y = 0.05$  and  $0.08$  with intensities of roughly  $\frac{1}{4}$  and  $\frac{1}{10}$ , respectively. The lattice parameters are increased to  $5.444 \pm 0.001$  and  $5.446 \pm 0.001$  Å for  $y = 0.05$  and  $0.08$ , respectively.

Nonstoichiometric  $\text{UO}_{2+x}$  splits into two cubic phases,  $\text{UO}_{2+x'}$  and  $\text{U}_4\text{O}_{9-y}$ , where  $x'$  is a small positive value, on slow cooling from high temperatures. The cooling rate in the present experiments was not sufficiently fast to retain the specimens in quenched state. In fact, the  $\text{UO}_{2+x}$  ( $x = 0.203$ ) heated at 1300°C in the same boat together with the solid solutions exhibited two phases with lattice parameters 5.4686 and 5.4442 Å. Therefore, it is probably correct to regard the phase separation at  $y = 0.005$  as being based on the same mechanism as  $\text{UO}_{2+x}$ . Conversely, the heating temperature in the present experiments fixes the  $x$  value of the solid solutions in equilibrium at that temperature. Phases obtained on cooling to room temperature might be those corresponding to temperatures considerably lower than the heating temperature.

The fact that the single-phase region exists at  $y \geq 0.01$  suggests that the strontium

ion has a stabilizing effect. The two phase regions near  $y = 0.03$ ,  $0.05$ , and  $0.08$  may be associated with the composition (or uranium valence) jumps. There are no two phases of the FCC structure below  $y = 0.33$  for  $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$  (4), but in  $\text{Ca}_y\text{U}_{1-y}\text{O}_{2+x}$  (6) a two-phase splitting occurs for  $y < 0.03$ , and for both phases the lattice parameter changes with  $y$ . This contradicts the phase rule which requires constancy of the lattice parameters. As a possible interpretation, disproportionation of  $\text{Ca}_y\text{U}_{1-y}\text{O}_{2+x}$  into  $\text{Ca}_y\text{U}_{1-y}\text{O}_{2+x_1}$  and  $\text{Ca}_y\text{U}_{1-y}\text{O}_{2+x_2}$  during relatively slow cooling process was considered (6).

Figure 5 shows the variation of lattice parameter with  $y$  in  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$  heated at 1300 and 1400°C. Except for the  $y = 0.005$  data (5.443-Å phase), the lattice parameters with an estimated uncertainty of  $\pm 0.0005$  Å are those of the 5.447-Å phase. If we smoothly connect the observed points,

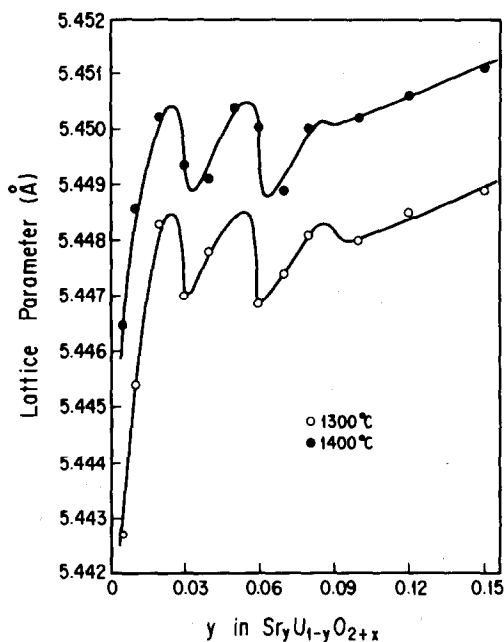


FIG. 5. Lattice parameter change as a function of  $y$  at low strontium concentrations (heated in He).  $\circ$ , 1300°C;  $\bullet$ , 1400°C.

three maxima are obtained for each curve which in the 1400°C curve coincide with the  $y$  values where the small amounts of the 5.443-Å phase appeared along with the 5.447-Å phase (see Fig. 4). As will be seen later, the lattice parameter decreases with increasing  $x$ . The  $x$  values of the 5.443-Å phase would therefore be higher than those of the 5.447-Å phase. Then, as long as the 5.443-Å phase coexists with the 5.447-Å phase, the latter should deviate toward the larger lattice parameter side, as is consistent with observation. Due to uncertainties in the lattice parameters, it is unclear whether they change with  $y$  close to  $y = 0.03, 0.05, \text{ and } 0.08$  (in two-phase regions). The parameter change, if observed, could be explained by considering the cooling process as yielding  $\text{Ca}_y\text{U}_{1-y}\text{O}_{2+x}$ .

The rapid decrease in lattice parameters at  $y = \text{ca. } 0.03, 0.06, \text{ and } 0.09$  is correlated with the jumps in the  $x$  value and the uranium valency. The crystal structure of the rhombohedral phase can be regarded as a slightly deformed cubic fluorite structure (18) with a partial ordering of strontium among the metal sites of the rhombohedral cell. Therefore, the discontinuities in  $x$  and in uranium valency for samples heated at 1200°C may be caused from stepwise hierarchical ordering of the strontium atoms. The steep change in the  $x$  value, uranium valency, and lattice parameter for the samples heated at 1300 and 1400°C may represent a residual effect (19) of the rhombohedral ordering, since this phase is not formed on heating at 1300 and 1400°C.

Thorn (19) has studied the thermodynamics of the residual structure as a function of temperature. The isotherm for activity vs composition is flat in the diphasic region. It is no more flat at higher temperatures than the critical temperature, but there still remains an inflection which is caused from the residue of the diphasic region. The microsource which generates this "degenerate" homogeneity is the thermal vibrations

of the atoms which tend to smear out the symmetry elements of the two structures. The nature of the residue itself was left unspecified but should comprise the decomposed microdomains (20, 21) from the initial two phases. These have been described in terms of the thermodynamics of small systems (22) leading to broad probability functions. The ordering and phase behavior of the  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$  above the critical temperature  $T_c$  may be discussed on essentially the same basis as used by Thorn.

The mechanism of formation of the rhombohedral phase has not been ascertained. Some excess oxygen is necessary, but the  $\text{Sr}^{2+}$  ion with a larger crystal radius than  $\text{Mg}^{2+}$  and/or  $\text{Ca}^{2+}$  is also needed. Leaving out the role of excess oxygen in the bonding scheme of the rhombohedral crystal, we discuss the strontium ordering by means of Bragg-Williams approximation. An order-disorder calculation has been reported for excess oxygen in  $\text{UO}_{2+x}$  (23); the present treatment is different in that we deal with an ordering of metals in the metal sites.

If  $N$ ,  $n_{\text{Sr}}$ , and  $n_{\text{U}}$  are the numbers of metal, strontium, and uranium sites, respectively, then

$$n_{\text{Sr}} + n_{\text{U}} = N. \quad (3)$$

Then, if the numbers of strontium and uranium atoms are given by  $N_{\text{Sr}}$  and  $N_{\text{U}}$ , respectively, and if there are no vacant metal sites,

$$N_{\text{Sr}} + N_{\text{U}} = N \quad (4)$$

$$x_{\text{Sr}} = \frac{N_{\text{Sr}}}{N_{\text{Sr}} + N_{\text{U}}} = \frac{n_{\text{Sr}}}{n_{\text{Sr}} + n_{\text{U}}} \quad (5)$$

$$x_{\text{U}} = \frac{N_{\text{U}}}{N_{\text{Sr}} + N_{\text{U}}} = \frac{n_{\text{U}}}{n_{\text{Sr}} + n_{\text{U}}}, \quad (6)$$

where  $x_{\text{Sr}}$  and  $x_{\text{U}}$  are the strontium and uranium atom fractions, respectively. Let the order parameter be  $X$ . The  $X$  values 1 and 0 define the ordered and disordered states,

respectively. If the number of strontium atom on the uranium sites is written as [Sr/U] etc., the following relations hold:

$$\begin{aligned} \left[ \frac{\text{Sr}}{\text{Sr}} \right] &= \{(1 + x_{\text{Sr}})X + x_{\text{Sr}}\}n_{\text{Sr}}, \\ \left[ \frac{\text{Sr}}{\text{U}} \right] &= (1 - x_{\text{U}})(1 - X)n_{\text{U}}, \\ \left[ \frac{\text{U}}{\text{Sr}} \right] &= (1 - x_{\text{Sr}})(1 - X)n_{\text{Sr}}, \\ \left[ \frac{\text{U}}{\text{U}} \right] &= \{(1 - x_{\text{U}})X + x_{\text{U}}\}n_{\text{U}}. \end{aligned} \quad (7)$$

Because of the low strontium concentration in the present compound, it may be assumed that for the ordered state no two strontium sites are adjacent. The interaction energy,  $E$ , due to nearest-neighbor metal atoms, is

$$\begin{aligned} E &= v_{\text{SrSr}} \left\{ \left[ \frac{\text{Sr}}{\text{Sr}} \right] \left[ \frac{\text{Sr}}{\text{U}} \right] + \left[ \frac{\text{Sr}}{\text{U}} \right] \left[ \frac{\text{Sr}}{\text{U}} \right] \right\} \\ &+ v_{\text{UU}} \left\{ \left[ \frac{\text{U}}{\text{Sr}} \right] \left[ \frac{\text{U}}{\text{U}} \right] + \left[ \frac{\text{U}}{\text{U}} \right] \left[ \frac{\text{U}}{\text{U}} \right] \right\} \\ &+ v_{\text{SrU}} \left\{ \left[ \frac{\text{Sr}}{\text{Sr}} \right] \left[ \frac{\text{U}}{\text{U}} \right] + \left[ \frac{\text{Sr}}{\text{U}} \right] \left[ \frac{\text{U}}{\text{U}} \right] + \left[ \frac{\text{Sr}}{\text{U}} \right] \left[ \frac{\text{U}}{\text{Sr}} \right] \right\}, \end{aligned} \quad (8)$$

where  $v_{\text{SrSr}}$ ,  $v_{\text{SrU}}$ , and  $v_{\text{UU}}$  are the Sr-Sr, Sr-U, and U-U interaction energies, respectively.

The configurational entropy  $S$  for order-disorder reads

$$S = k \cdot \ln \left\{ \frac{n_{\text{Sr}}!}{\left[ \frac{\text{Sr}}{\text{Sr}} \right]! \left[ \frac{\text{U}}{\text{Sr}} \right]!} \frac{n_{\text{U}}!}{\left[ \frac{\text{Sr}}{\text{U}} \right]! \left[ \frac{\text{U}}{\text{U}} \right]!} \right\}. \quad (9)$$

The equilibrium state is attained for

$$\frac{\partial F}{\partial X} = 0, \quad (10)$$

where  $F = E - TS$ . The above derivatives can be calculated after substitution of Eq. (7) into Eqs. (8) and (9). A series expansion of the logarithmic term near  $X = 0$  leads to

$$\begin{aligned} -\frac{z}{kT} \cdot A + \left( -\frac{z}{kT} \cdot B + 1 \right) X \\ - \frac{(1 - 2x_{\text{U}})^2}{2x_{\text{U}}(1 - x_{\text{U}})} X^2 + \dots = 0, \end{aligned} \quad (11)$$

where  $z (= 12)$  is the coordination number, and

$$A = (1 - x_{\text{U}})\{(1 - x_{\text{U}})\{(1 - x_{\text{U}})v_{\text{SrSr}} - x_{\text{U}}v_{\text{UU}}\} + (2x_{\text{U}} - 1)(x_{\text{U}} + 1)v_{\text{SrU}}\} \quad (12)$$

$$B = x_{\text{U}}(1 - x_{\text{U}})\{(1 - x_{\text{U}})(v_{\text{SrSr}} + v_{\text{UU}}) - 2v_{\text{SrU}}x_{\text{U}}\}. \quad (13)$$

The critical point is obtained by

$$-\frac{z}{kT} \cdot B + 1 = 0. \quad (14)$$

If  $T_c = 1473$  K is taken as the critical temperature, and if ordering at  $x_{\text{U}} = 0.94$  is examined, since interactions ( $v_{\text{SrSr}} + v_{\text{UU}}$ ) would be of the same order of magnitude as  $2v_{\text{SrU}}$ , the first term in the square brackets of the right-hand side of Eq. (13) can be neglected due to the smallness of  $(1 - x_{\text{U}})$ . By putting this  $B$  value in Eq. (14), one has

$$v_{\text{SrU}} = -9.6 \text{ kJ} \cdot \text{mole}^{-1}. \quad (15)$$

The first term in the square brackets of Eq. (12) can also be neglected compared to the second term. Using the value of Eq. (15), the first term in Eq. (11) is calculated to be 0.96 for  $T_c = 1473$  K. The order parameter  $X$  just below  $T_c$  is obtained as

$$X = 0.37, \quad (16)$$

neglecting terms of order greater than  $X^2$  in Eq. (11).

The partial ordering seems to be reasonable in reference to the crystal structure of the rhombohedral phase (18). The X-ray diffraction lines are consistent with an ordered structure for  $x_{\text{Sr}} = 0.125$ . The X-ray observations are rationalized if the  $x_{\text{Sr}} = 0.06$  structure is assumed to be formed by random occupation of the strontium sites of the (hypothetical)  $x_{\text{Sr}} = 0.125$  structure with



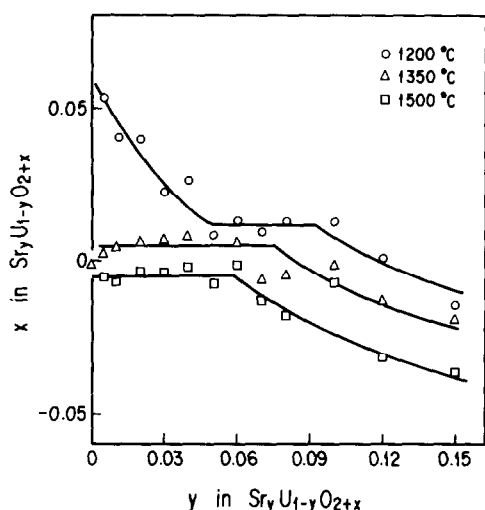


FIG. 6. Variation of  $x$  value in  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$  with  $y$  for samples heated in vacuum.  $\circ$ , 1200°C;  $\triangle$ , 1350°C;  $\square$ , 1500°C.

strontium and uranium atoms in the ratio 0.06: (0.125–0.06).

The low rate of approach to equilibrium is noteworthy. The  $x$  value in  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$  changed considerably at the first heating cycle of 50 hr at 1300°C, but still changed slightly even on the third heating. Apparently, the diffusion of the large  $\text{Sr}^{2+}$  into the metal sites of the crystal is low.

## 2. Reaction in Vacuum

Mixtures with bulk composition  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2.10}$  were heated in a dynamic vacuum of  $1 \times 10^{-6}$  Torr  $\text{O}_2$  for 50 hr. Figure 6 represents the variation of the  $x$  values with strontium concentration; all products were face centered cubic. The  $x$  values are all negative when the samples were heated at 1500°C. For heat treatments at 1350 and 1200°C,  $x$  is negative in the ranges  $0.07 \leq y \leq 0.15$  and at  $y = 0.15$ , respectively. The smallest  $x$  value is  $-0.036$  for  $y = 0.15$  at 1500°C. The  $x$  value of 1200°C samples decreases with  $y$  up to  $y = 0.05$ , and remains almost flat between 0.05 and 0.09, then decreases further for  $y > 0.09$ . For 1350 and

1500°C samples, the flat region extends and spreads to the lower  $y$  side. Both of the latter curves are similar in shape. There are no clear  $x$  jumps for samples heated in vacuum for which the  $x$  values are lower than those of specimens heated in helium.

The change of mean uranium valency of the products is shown in Fig. 7 as a function of  $y$ . For the 1200°C samples, the slope changes at  $y = 0.06$ . The slope above  $y = 0.06$  is almost the same as those of the samples heated at 1350 and 1500°C in the region higher than ca. 0.07. The slope for the 1200°C samples is lower at  $y < 0.06$ . In 1350 and 1500°C curves, flat regions exist for  $y = 0.06$ . This result may be related with the initial stage of formation of the rhombohedral phase at larger  $x$  values.

Figure 8 shows the lattice parameter change as a function of  $y$ . The three curves in the figure decrease with increasing  $y$ , in contrast to Figs. 1 and 5; this discrepancy is due to oxygen nonstoichiometry. The rapid

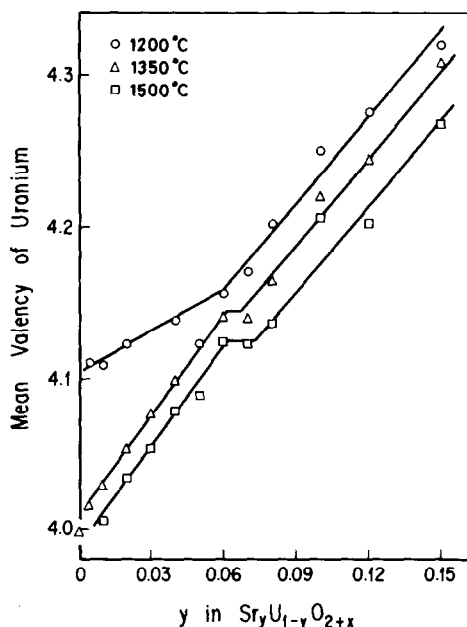


FIG. 7. Mean valency of uranium in the samples heated in vacuum.  $\circ$ , 1200°C;  $\triangle$ , 1350°C;  $\square$ , 1500°C.

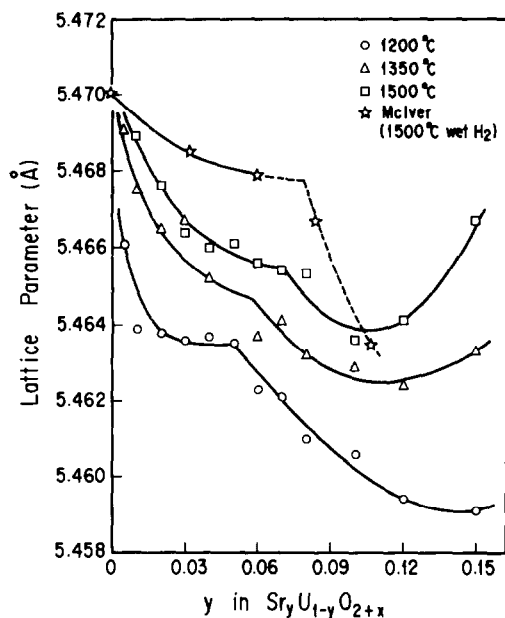


FIG. 8. Lattice parameter as a function of  $y$  for samples heated in vacuum.  $\circ$ , 1200°C;  $\triangle$ , 1350°C;  $\square$ , 1500°C.  $\star$ , Literature values for the samples heated in wet  $\text{H}_2$  ( $\Delta\bar{G}_{\text{O}_2} = -110 \text{ kcal}_{\text{th}} \cdot \text{mole}^{-1}$ ) (9).

decrease of the lattice parameter in the range of small  $y$  in this case is caused by a rapid increase of  $x$  in  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$ . The curves are concave, and show anomalies, although they do not exhibit any jumps. The  $y$  value for the anomaly increases from 0.05 (1200°C curve) to 0.07 (1500°C curve) and becomes more accentuated at 1200°C. For the 1350 and 1500°C samples, the lattice parameter again increases for  $y > 0.10$ . Compared to McIver (9), our lattice parameters are lower, which shows that the  $x$  values of McIver's samples were smaller, as is reasonable because of his heating in wet hydrogen at 1500°C. It is notable that the same anomaly is observed also in his curve.

The lattice parameter curves, shown in Figs. 1, 5, and 8 as a function of  $y$ , contain the change of  $x$  implicitly. To express the effect of  $x$  and  $y$  separately, least-squares calculations were carried out on adopting the parameter 5.4704 Å (24) at  $x = y = 0$ .

The single phase FCC lattice parameters and compositions were used. The results are:

$$a = 5.4704 - 0.109x - 0.098y$$

(in Å for  $x \geq 0$ ) (17)

and

$$a = 5.4704 - 0.244x - 0.098y$$

(in Å for  $x < 0$ ). (18)

These equations show that the lattice parameter diminishes with increasing  $x$  and  $y$ . First, we examine the coefficient of  $x = -0.109$  in Eq. (17) which is comparable with  $-0.127$ ,  $-0.10$ ,  $-0.117$ , and  $-0.094$  for  $\text{Pr}_y\text{U}_{1-y}\text{O}_{2+x}$  (25),  $\text{Nd}_y\text{U}_{1-y}\text{O}_{2+x}$  (26),  $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$  (4), and  $\text{UO}_{2+x}$  (24), respectively. Since coefficients of this order of magnitude are characteristic of the fluorite defect structure with oxygen interstitials (27), the oxygen nonstoichiometry in the range  $x > 0$  for the present strontium solid solution can be regarded as involving interstitialcy.

The coefficient of  $x$  for the range  $x < 0$  is  $-0.244$ , which is fairly well consistent with  $-0.30$ ,  $-0.24$ , and  $-0.28$  for  $\text{Nd}_y\text{U}_{1-y}\text{O}_{2+x}$  (26),  $\text{Gd}_y\text{U}_{1-y}\text{O}_{2+x}$  (28), and  $\text{La}_y\text{U}_{1-y}\text{O}_{2+x}$  (29), respectively. By analogy with the defect types of these compounds, the strontium solid solution is considered to have oxygen vacancies in the range  $x < 0$ .

The coefficient of  $y$  is  $-0.098$ , which is largest (negatively smallest) in the solid solutions  $\text{M}_y\text{U}_{1-y}\text{O}_{2+x}$  ( $M = \text{Mg}, \text{Ca}, \text{and Sr}$ ). A plot of these coefficients against crystal radii of the divalent alkaline earth ions with coordination number 8 (30) is linear; its slope differs from that for another straight line for trivalent lanthanides. However, both the lines can be reformed into a single straight line if the following plot is made.

Consider the case of  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$  as an example. If one  $\text{U}^{4+}$  (1.14 Å, CN = 8) atom is replaced by  $\text{Sr}^{2+}$  (1.40 Å, CN = 8), the crystal radius increases by 0.26 Å; whereas

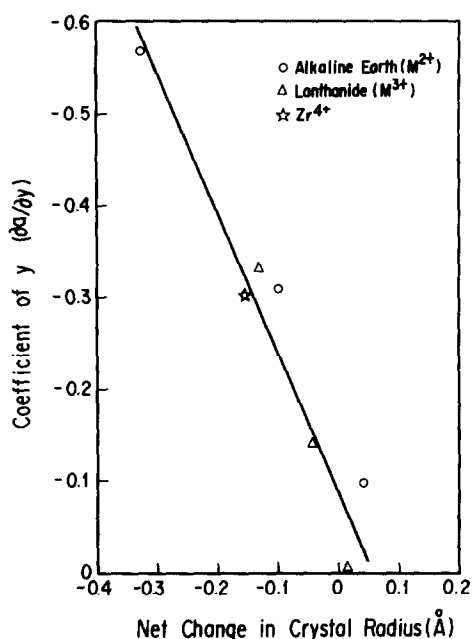


FIG. 9. Plot of coefficient of  $y$  as a function of net change in the crystal radius. Literature data:  $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$  (4),  $\text{Ca}_y\text{U}_{1-y}\text{O}_{2+x}$  (6),  $\text{M}_y\text{U}_{1-y}\text{O}_{2+x}$  with  $M = \text{Lu}$ ,  $\text{Eu}$ , and  $\text{Pr}$  (25), and  $\text{Zr}_y\text{U}_{1-y}\text{O}_{2+x}$  (31).

two  $\text{U}^{4+}$  atoms oxidized to  $\text{U}^{5+}$  ( $1.03 \text{ \AA}$ , CN = 8) for valence compensation cause a  $(1.14-1.03) \times 2 = 0.22 \text{ \AA}$  decrease in crystal radius. The net change of crystal radius should be an increase of  $0.04 \text{ \AA}$ . For trivalent lanthanides, only one uranium atom is oxidized. Figure 9 indicates the change of the coefficient of  $y$  as a function of the net change in the crystal radius. The coefficients for both alkaline earth metals and lanthanides are on a straight line. In this figure, the coefficients for the solid solutions of lanthanides were taken from the literature, i.e.,  $-0.5677$ ,  $-0.310$ ,  $-0.3332$ ,  $-0.1404$ , and  $-0.007$  for  $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$  (4),  $\text{Ca}_y\text{U}_{1-y}\text{O}_{2+x}$  (6),  $\text{Lu}_y\text{U}_{1-y}\text{O}_{2+x}$  (25),  $\text{Eu}_y\text{U}_{1-y}\text{O}_{2+x}$  (25), and  $\text{Pr}_y\text{U}_{1-y}\text{O}_{2+x}$  (25), respectively. Europium and praseodymium in the above solid solutions have been shown to be trivalent (25). The value for tetravalent zirconium (31) is also depicted. The change of the coefficient of  $y$  is seen to be

well-expressed in one straight line, irrespective of the valency of the foreign cation. The increase of the coefficient is 1.500 per  $1\text{-\AA}$  increase of the net change in crystal radius.

The formation reaction of the magnesium solid solution,  $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$  (4), is faster than the present solid solution, and the coefficient for  $\text{Mg}_y\text{U}_{1-y}\text{O}_{2+x}$  ( $-0.5677$ ) is much smaller than that for  $\text{Sr}_y\text{U}_{1-y}\text{O}_{2+x}$ . If we compare the larger crystal radius of  $\text{Sr}^{2+}$  ( $1.40 \text{ \AA}$ ) with that of  $1.03 \text{ \AA}$  of  $\text{Mg}^{2+}$ , the slow diffusion of strontium in the fluorite lattice is understandable. The radius for  $\text{U}^{4+}$  is  $1.14 \text{ \AA}$ . However, it is dubious whether one can directly relate the lower stability of the solid solution to the coefficient of  $y$ .

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