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INVESTIGATIONS IN THE SYSTEM URANIA-NEODYMIA

by

D. Kolar,* J. H. Handwerk, and R. J. Beals

Metallurgy Division

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* At the time of this work, D. Kolar was a participant in the International Institute of Nuclear Science and Engineering at ANL and is now at the Institute Josef Stefan, Ljubljana, Yugoslavia.

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ABSTRACT

Urania-neodymia compositions were sintered in air and in hydrogen. The compositions were studied by chemical, X-ray, and differential thermal analyses. Solid solutions formed readily in air-sintered compositions in the range from 20 to 60 m/o Nd_2O_3 . Solid solutions formed slowly and incompletely, up to 1650°C , in hydrogen-sintered compositions. There was good correlation between the differential thermal analyses and the chemical and X-ray analyses.

INTRODUCTION

The growth of nuclear technology for power reactor applications stimulated the investigation of urania as a fuel material. It was found that, at elevated temperatures, UO_2 oxidized to nonstoichiometric U_3O_8 with a resultant disruptive increase in volume, with an increase in vapor pressure, and a lowering of fission product retention and irradiation stability.⁽¹⁾ The development of thoria-urania^(2,3) and of zirconia-calcia-urania⁽⁴⁾ compositions for use as nuclear fuels heightened interest in other oxide systems which might improve the high-temperature stability of urania in oxidizing environments or which might otherwise enhance the properties of UO_2 as a fuel.

The oxides of interest are those which form extensive solid solutions with urania. From the oxides reported in the literature,^(5,6) neodymium oxide was selected for this study. This oxide has a moderate thermal-neutron cross section (46 b) and is relatively abundant. Hund and Peetz⁽⁵⁾ and Lambertson and Mueller⁽⁶⁾ have investigated the solid solutions in the system $\text{UO}_2\text{-Nd}_2\text{O}_3$. These solid solutions were prepared either by reacting Nd_2O_3 with UO_2 in a protective atmosphere or by reacting codigested nitrates in air. Hund and Peetz⁽⁵⁾ indicated that fluorite-structured solid solutions were formed in air-sintered mixtures in the range from 25 to 65 m/o Nd_2O_3 . Lambertson and Mueller⁽⁶⁾ found that, with hydrogen sintering, the Nd^{+3} ion could be substituted extensively for the U^{+4} ion in the fluorite-type solid solutions. They concluded that the

UO₂-Nd₂O₃ system has a rather unusual solid solution behavior for ceramic oxides. As Nd⁺³ is substituted for U⁺⁴ in the face-centered-cubic lattice, an oxygen deficiency must be created or some U⁺⁴ must be oxidized to U⁺⁶ so that the balance of charges is maintained. These previous investigations were concerned with the limits of solid solubility and the phase relationships of the binary system. This investigation was undertaken to study the formation of the solid solutions and the stabilization of the UO₂ fluorite-type structure in an oxidizing atmosphere.

EXPERIMENTAL PROCEDURE

Sample Preparation

Compositions of varying proportions of UO₂* and Nd₂O₃** were dry mixed for 4 hr in a rubber-lined mill. The compositions, formulated to give mole percentages of neodymia from 5% to 95%, were pelletized at a pressure of 14,000 psi and were sintered in hydrogen or in air atmospheres. The sintering temperature of 1650°C was reached slowly overnight, followed by a 4-hr soak at temperature. Following furnace cooling to room temperature, the sintered material was crushed to a fine powder and stored in sealed bottles.

Chemical and X-ray Analysis

The powders of each composition were analyzed chemically for total uranium, for U⁺⁴, and for neodymium content, with accuracies of >±0.1% for uranium and of >±0.5% for neodymium. Stoichiometries of the compositions were calculated on the assumption that the neodymium ion existed in the trivalent state.

X-ray diffraction patterns were made of the powdered samples with CuKα radiation with a 114.59-mm-diameter camera. The X-ray patterns were taken for both the hydrogen-sintered and air-sintered mixtures: (a) immediately after crushing, (b) after three-month storage in powdered form in air, and (c) after low-temperature DTA examination (up to 650°C in dynamic oxygen). Selected powders which had been hydrogen sintered at 1650°C were resintered in air for 4 hr at 1400°C to study the effects of this treatment on the stability of the lattice parameters of the solid solutions.

*Spencer depleted "Ceramic Grade," UO_{2.063}, Lot No. 2926.

**Lindsay Chemical Division Nd₂O₃, Code 6299, Lot LPO920.

The 114.59-mm camera is designed so that the film distance between 2θ values of 0° and 180° is 180 mm. By measuring the film distances on a Norelco pattern analyzer and correcting for film shrinkage, a direct reading of the Bragg angle was possible. The small angles were used to classify the patterns, and the large angles, near 180° , were used to determine the lattice parameters of the crystals.

Graphical extrapolation methods or the least-squares method can be used to obtain the most reliable values of lattice parameters for the crystals. The method outlined by Mueller and Heaton,⁽⁷⁾ a least-squares analytical extrapolation, was used in determining on the IBM-704 Computer* the lattice parameters for the urania-neodymia compositions.

Data supplied to the computer included the measured angle, in degrees, corresponding to each line; the α_i value which corresponds to the sum of the squares of the Miller indices ($h^2 + k^2 + l^2$) for each line; the wavelength of the radiation for each observation; the observation weight for each measured line, which in this analysis was given an initial value of unity; the number of observations; a starting value for A_0 for the lattice; as well as drift constants, trigonometric functions to be used with the drift constants, and the type of trigonometric weighting factor to be used.

By carrying out a number of different solutions, it should be possible to detect the presence of systematic errors, to determine the most suitable type of systematic correction, and to judge the fit of the lattice parameters to the supplied data.

Six solutions were used for each set of data to determine lattice parameters. The solutions employed were:

1. No systematic correction with equal weight for all observations (AW^1), in which A corresponds to the cubic system and W^1 represents no observational or trigonometric weighting, or a weight, w , of one for each line.
2. No systematic correction with weighted values for the lines (AW^2), in which W^2 indicates a weight of $w/\sin^2 2\theta$ for each observation, which is the usual weighting for the Debye-Scherrer camera.
3. A systematic correction with equal weight (AD^1W^1) in which D^1 corresponds to a trigonometric correction of $\sin^2 2\theta$.

*The determination of precise lattice parameters was programmed for the IBM-704 Computer by W. G. Greenhow of the Applied Mathematics Division, Argonne National Laboratory.

4. A systematic correction with weighted values for the lines (AD^1W^2).
5. A second systematic correction with equal weighting (AE^2W^1) in which E^2 corresponds to a correction of $[(1/\sin \theta) + (1/\theta)] \sin^2 2\theta$.
6. A systematic correction with weighted values for the lines (AE^2W^2).

The present program on the IBM-704 provides for a print out of the input data; lattice parameters and standard errors; the " v " for each observation, which is the difference between $\sin^2 \theta$ (observed) and $\sin^2 \theta$ (calculated); and the standard deviation, σ^2 , of the observed values from the calculated values. Further details on the method are given in the Appendix.

Differential Thermal Analysis

Differential thermal analysis curves were obtained for the hydrogen-sintered and air-sintered powders by the dynamic flow gas method described by Stone.⁽⁸⁾ The standard against which the powders were compared was fused alumina. An oxygen flow of approximately 20 cc/min was maintained throughout the determination. A heating rate of 10°C/min was used to bring the powders to the ultimate temperature of 650°C.

RESULTS AND DISCUSSION

Solid solutions formed readily in air-sintered mixtures of UO_2 and Nd_2O_3 within the approximate composition limits of 20 to 60 m/o neodymia. The presence of the face-centered-cubic fluorite-type structure was confirmed by X-ray examination. The phases identified are shown in Table I. A faint X-ray diffraction pattern corresponding to the fluorite-type structure was obtained at neodymia contents of 5 m/o. The intensities of the diffraction lines for the cubic structure increased in the 10 m/o neodymia whereas the intensity decreased for the orthorhombic U_3O_8 . At 20 m/o neodymia, a slight indication of U_3O_8 was present. Above this composition, only the face-centered-cubic solid solution was detected.

The lattice parameter of the solid solution increased with increasing neodymia content, changing from 5.430 a.u. at 20 m/o neodymia to 5.451 a.u. at 60 m/o neodymia. The change of parameter with composition is shown in Table I and Figure 1. Hund and Peetz⁽⁵⁾ found parameters ranging from 5.434 a.u. at 25 m/o Nd_2O_3 to 5.448 a.u. at 60 m/o Nd_2O_3 . These data are also plotted in Figure 1.

Table I

X-RAY AND CHEMICAL ANALYSES OF URANIA-NEODYMIA SOLID SOLUTIONS

Specimen No.	Analyzed Composition			Mole % Nd ₂ O ₃	Calculated Atomic Ratio		X-Ray Investigation of Powder Samples		
	w/o U	w/o U+4	w/o Nd		Oxygen to Metal	Oxygen to Uranium	Lattice Parameter (Å)		Phases Present
							As Sintered	After 3-month Air Exposure	
	Heat Treatment: Combustion Atmosphere at 1650°C for 4 hr								
A3N05	-	-	-	ca 5	-	-	-	-	Orthorhombic U ₃ O ₈ + Slight F.C.C. F.C.C. + Slight U ₃ O ₈
A4N10	79.77 79.88	39.57 39.05	5.75 5.83	10.62 10.74	2.399 2.402	2.504 2.534	5.432 ± 0.001 -	5.430 ± 0.001 -	
A5N20	74.52	41.99	11.60	20.44	2.245	2.436	5.430 ± 0.001	5.430 ± 0.001	F.C.C. + v.s. U ₃ O ₈
A6N30	67.74	34.44	17.95	30.42	2.190	2.492	5.435 ± 0.001	5.435 ± 0.001	
A7N40	60.56	27.60	25.0	40.52	2.121	2.544	5.442 ± 0.001	5.442 ± 0.001	F.C.C.
A8N50	53.14	24.29	32.6	50.31	2.018	2.543	5.447 ± 0.001	5.447 ± 0.001	F.C.C.
	52.95	24.58	32.59	50.39	2.016	2.506	-	-	
A9N60	45.08	12.21	40.2	59.54	1.997	2.729	5.451 ± 0.001	5.450 ± 0.001	F.C.C.
A10N70	36.39	0.681	48.7	68.84	1.961	2.981	5.473 ± 0.001	5.472 ± 0.001	F.C.C.
	Heat Treatment: Hydrogen Atmosphere at 1650°C for 4 hr								
E4N05	-	-	-	ca5	-	-	-	5.470 ± 0.001	UO ₂
E13N10	80.42	72.09	8.31	14.56	2.016	2.104	5.470 ± 0.001	5.470 ± 0.001	UO ₂ + F.C.C.
E14N20	-	-	-	ca20	-	-	5.467 ± 0.001	5.459 ± 0.001	F.C.C. + UO ₂
E10N30	69.59	55.09	17.44	28.57	2.001	2.208	5.449 ± 0.001	5.451 ± 0.001	F.C.C. + v.s. UO ₂
E6N40	61.86	42.40	24.99	40.00	1.990	2.314	5.454 ± 0.001	5.452 ± 0.001	F.C.C.
E11N50	54.25	30.16	31.8	49.16	1.979	2.444	5.450 ± 0.001	5.451 ± 0.001	F.C.C.
E5N60	-	-	-	ca 60	-	-	5.457 ± 0.001	5.455 ± 0.001	F.C.C.
E12N70	35.86	13.86	49.9	69.67	1.838	2.613	5.521 ± 0.001	5.521 ± 0.001	F.C.C. + F.C.C. ("C" type)
E7N80	25.34	11.52	59.39	79.46	1.715	2.545	5.523 ± 0.001	5.528 ± 0.001	F.C.C. ("C" type) + s. hexag
E8N90	13.97	7.33	73.2	89.65	1.601	2.475	-	-	Hexag + s. F.C.C. ("C" type)
E3N95	7.08	3.70	77.20	94.74	1.551	2.478	-	-	Hexag + v.s. F.C.C. ("C" type)

The complete data for the different solutions of the lattice parameters, the probable errors in the parameters, and the standard deviations

between observed and calculated data are given in the Appendix. Examples of the effect of systematic errors upon the lattice parameters and the improvement brought about by systematic corrections are illustrated.

Figure 1. Lattice Parameters for Air-exposed Urania-Neodymia Solid Solutions.

lishes the solid-solution limits.

The upper limit of solid-solution formation was approximated by extrapolation. At 70 m/o neodymia the fluorite-type structure was still present. The distorted nature of the structure at this composition was shown by the blackening of the X-ray film and by the deviation of the parameter value from the straight line (in Figure 2) at the oxygen-to-metal atomic ratio of 1.961. The linear relationship between lattice parameter and oxygen-to-metal atomic ratio in the ratio range from 2.245 to 1.997 further estab-

Solid solutions of UO_2 and Nd_2O_3 were not readily formed when compositions were sintered in a hydrogen atmosphere at 1650°C for 4 hr.

Figure 2. Variation of Lattice Parameter with Oxygen/Metal Atomic Ratio for Air-exposed Urania-Neodymia Solid Solutions

The fluorite structure of UO_2 was evident, from X-ray examination, up to 30 m/o neodymia. The solid solutions formed below 30 m/o neodymia had lattice parameters from 5.467 to 5.470 a.u. (see Table I) which are close to that of pure UO_2 , with a parameter of 4.467.

In the compositional region near 30 m/o neodymia, a different face-centered-cubic solid solution (reversal solution) was observed. The slightly smaller lattice parameters of these reversal solutions, 5.449 to 5.457 a.u., increased as the Nd_2O_3 content increased, as may be observed in Figure 1.

Between 30 and 60 m/o neodymia a single solid solution was found to be present. At 70 m/o Nd_2O_3 , a second face-centered-cubic structure, with a lattice parameter of 5.521 a.u., was evident. This value is close to the reported value^(5,6,9) of 5.53 a.u. for the cubic substructure of the "C"-type rare earths. The predominant phase observed at 80 m/o Nd_2O_3 was the "C"-type structure. A small amount of a hexagonal phase was observed. This could have been either an "A" type of rare earth or a hydrolyzed product of Nd_2O_3 . As differential thermal analysis showed, the hydrolyzed $\text{Nd}(\text{OH})_3$ was formed. Joye and Garnier⁽¹⁰⁾ reported the existence of this hydrolysis in neodymia.

Above 80 m/o Nd_2O_3 , increasing intensity of the diffraction lines corresponding to the hexagonal structure was observed. The work of Lambertson and Mueller⁽⁶⁾ on the phase diagram of the system urania-neodymia corroborates these data. They reported the face-centered-cubic phase to exist up to 78 m/o Nd_2O_3 and the hexagonal phase to exist at higher neodymia contents.

Three months passed between the formulation of the solid solutions and the completion of chemical analyses. The aged powders were examined by X-ray diffraction to determine the effect of air exposure on the solid solution parameters. There was no appreciable change in the lattice parameters of the air-sintered compositions, as may be seen in Table I. The lattice parameters of the hydrogen-sintered solid solutions decreased, to a limited extent, after exposure.

Selected samples, which had been sintered in hydrogen, were resintered in air at 1400°C for 4 hr. The lattice parameters of the solid solutions formed by this treatment were close to the parameters of the original air-sintered samples. These data are given in Table II and are plotted in Figure 1.

Table II

LATTICE PARAMETER CHANGES IN RESINTERING
HYDROGEN-SINTERED SOLID SOLUTIONS

Nominal Sample Composition (m/o Neodymia)	Lattice Parameters, Å	
	Hydrogen Sintered (1600°C for 4 hr)	Air Resintered (1400°C for 4 hr)
10	5.470	5.437
30	5.449	5.431
50	5.450	5.447

Anderson *et al.*,⁽¹¹⁾ and Ferguson and Fogg⁽¹²⁾ suggest that the UO_2 -containing cubic fluorite-type solutions have vacancies in the anion sublattice. They observed that such vacancies could be filled easily by oxygen if one of the cations can be oxidized. Similar behavior in the system UO_2 - Nd_2O_3 may be inferred by an examination of Figures 3 and 4.

Figure 3
Variation of Oxygen-to-Metal
Atomic Ratio for Urania-
Neodymia Solid Solutions

Figure 4
Variation of Oxygen-to-Uranium
Atomic Ratio for Urania-
Neodymia Solid Solutions

Significant amounts of U^{+6} ions are present in hydrogen-sintered samples which have been exposed to air. As the concentration of the neodymia increases, there is an increase in the amount of U^{+6} ions in the solid solution. In Figure 3, it may be observed that the oxygen-to-metal atomic ratio approaches the theoretical values for U_3O_8 . The U^{+6} ion concentration of hydrogen-sintered compositions increases almost linearly up to a composition of 66 m/o neodymia when plotting oxygen-to-uranium atomic ratio against neodymia content (see Figure 4).

As Nd^{+3} is substituted for U^{+4} in the cubic lattice, an oxygen deficiency is created. The oxidation of some of the remaining U^{+4} to U^{+6} will balance the valence deficiency, as suggested by Lambertson and Mueller.⁽⁶⁾ At 66 m/o Nd_2O_3 , all of the uranium ions would be in the higher valence state for an intact anion lattice. Further increases in the Nd_2O_3 content bring about the destruction of the face-centered-cubic structure. It is noteworthy that, up to approximately 50 m/o Nd_2O_3 , as shown in Figure 3, the total oxygen-to-metal atom ratio remains at approximately 2. This is above the neodymia content which would be expected by merely replacing U^{+4} ions with Nd^{+3} ions. Thus, indications are that the lattice is oxygen sufficient and corresponds to a solution of U_3O_8 and Nd_2O_3 . Air-sintered solutions were oxygen sufficient, as far as oxygen-to-uranium atom ratio in the U^{+4} ion fluorite-type lattice was concerned and oxygen deficient when compared with solutions of U_3O_8 and Nd_2O_3 . Neodymia appears to be beneficial in preserving the fluorite-type lattice. The amount of oxygen which appears to be necessary to fill the free spaces in the lattice varies with the heat treatment used and with the activity of the raw materials.

The thermal behavior of hydrogen-sintered solid solutions of UO_2 and Nd_2O_3 was investigated by differential thermal analysis. The curves obtained are shown in Figure 5. There is close agreement between these

Figure 5. DTA Curves for Different Urania-Neodymia Solid Solutions

data and the results of chemical and X-ray analyses reported in Table I. The double exothermic peaks evident at the low neodymia contents correspond to the two-stage oxidation of UO_2 to U_3O_7 (around 350°C) and of U_3O_7 to U_3O_8 (around 410°C).⁽¹³⁾ Above 30 m/o Nd_2O_3 , where no free urania exists, these peaks were not evident. X-ray diffraction analysis of the material after differential thermal analysis showed orthorhombic U_3O_8 and a face-centered-cubic phase.

The DTA curves for compositions of more than 80 m/o neodymia show two exotherms. These are at 310°C and at around 510°C . Joye and Garnier⁽¹⁰⁾ reported the thermal decomposition of $\text{Nd}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ to occur in two stages to give $2\text{Nd}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ at 310°C to 325°C and the decomposition of this hydrate at 500°C to 525°C to give $2\text{Nd}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (or $\text{Nd}_2\text{O}_3 \cdot \text{H}_2\text{O}$). The close agreement between the reported temperatures and the endothermal temperatures on the DTA traces establishes the hydrolyzation of the neodymia. This hydrolysis was evidently due to prolonged exposure to the atmosphere, since the analysis of the high-fired, freshly crushed neodymia gave no indication of the hydrate. The DTA curves for atmosphere exposed and for freshly sintered Nd_2O_3 powders are shown in Figure 6.

Figure 6. DTA Curves for Nd_2O_3

The lattice parameters of hydrogen-sintered urania-neodymia compositions which had been subjected to low-temperature (650°C) differential thermal analysis were determined. Within the limits of solid-solution formation there was a slight increase in the parameter after this exposure, as may be observed in Table III.

Table III

INFLUENCE OF LOW-TEMPERATURE DTA TREATMENT (650°C) ON
THE LATTICE PARAMETER OF HYDROGEN-SINTERED SAMPLES

Nominal Sample Composition (m/o Neodymia)	Lattice Parameter ($\text{\AA}$)	
	Before DTA Treatment*	After DTA Treatment
10	5.470	5.452
20	5.459	5.461
30	5.451	5.447
40	5.452	5.452
50	5.451	5.451
60	5.454	5.455
80	5.522	5.519

*These parameters are for samples which had been stored for 3 months in powder form.

An unreacted mixture of 50 m/o UO_2 and 50 m/o Nd_2O_3 was subjected to differential thermal analysis. The Nd_2O_3 had been freshly air sintered at 1000°C to obviate the endotherms associated with the hydrates of neodymia. The DTA trace is shown in Figure 7. A 10:1 magnification of the portion from 600°C to 1200°C is shown in Figure 8. A dynamic

Figure 7
DTA Curve of 50:50 m/o Mixture of
Unreacted UO_2 - Nd_2O_3

Figure 8
DTA Curve of 50:50 Mixture UO_2 -
 Nd_2O_3 ; Higher Amplification between
600-1200°C

stream of oxygen flowed through the sample and the standard during the test. The oxidation of UO_2 to U_3O_7 and to U_3O_8 is evident from Figure 7 in the two exotherms below 400°C .

Above 900°C , another exotherm is evident. This corresponds to the formation of the urania-neodymia solid solution. In this determination, the peak value occurred at 1050°C . Under slightly different conditions of sintering and sample preparation, the peak may occur at temperatures up to 1200°C .

X-ray analyses of samples heated to 800°C indicated the presence of orthorhombic U_3O_8 and hexagonal Nd_2O_3 . There were no indications of solid-solution formation. The face-centered-cubic solid solution was evident when samples heated to 1250°C were analyzed. This corroborates the findings from the differential thermal analysis. It is noteworthy that the formation of the solid solution is accompanied by the liberation of energy. This confirms the contention of Lambertson and Mueller⁽⁶⁾ that some of the U^{+4} must be oxidized to U^{+6} in order to maintain a balance of the charges when Nd^{+3} is substituted for U^{+4} in the face-centered-cubic lattice.

SUMMARY

Solid solutions of urania and neodymia form readily in an oxidizing atmosphere and slowly in a hydrogen atmosphere. The lattice parameter of air-sintered solid solutions increased linearly over the range from 20 to 60 m/o Nd_2O_3 . Free UO_2 was indicated by X-ray and differential thermal analyses in hydrogen-sintered samples containing up to 30 m/o Nd_2O_3 . Between 30 and 60 m/o Nd_2O_3 , only the face-centered cubic solid solution was present. Two structures, the face-centered cubic solid solution and the "C"-type rare earth oxide, were present at 70 m/o Nd_2O_3 . At 80 m/o Nd_2O_3 , the "C"-type Nd_2O_3 was the predominant phase, with indications of small amounts of a hexagonal phase which was probably hydrolyzed Nd_2O_3 . Above 80 m/o neodymia, the hexagonal phase increased while the "C"-type structure diminished. In solid solutions containing up to 50 m/o neodymia the hydrogen-sintered specimens were oxygen sufficient. The solid-solution formation for urania-neodymia occurs below 1200°C , with evidence of the resultant oxidation of U^{+4} to U^{+6} .

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APPENDIX

ANALYSIS OF X-RAY DIFFRACTION PATTERNS BY THE LEAST-SQUARES EXTRAPOLATION METHOD

Lattice parameters of crystalline materials determined by an analysis of one or more diffraction lines may be subject to considerable variance and/or error. It is possible, by graphical extrapolation, to minimize the errors. By carrying out an analytical extrapolation with the method of least squares, it is possible to eliminate⁽⁷⁾ subjective errors which occur when a curve is fitted to a set of points, and it is possible to use more observed data in determining the parameters.

Because of the large number of calculations which must be made with the method of least squares, the use of a calculator is advisable. The procedure for making the parameter determinations is reproduced here, in some detail, to give insight into the applications of this technique to specific problems. The material herein is based upon the work of Mueller and Heaton⁽⁷⁾ and upon personal communications with these investigators.

The lines in the back-reflection region of the X-ray diffraction film, corresponding to Bragg angles between 56° and 83° , were used in the analyses. The patterns were obtained with $\text{CuK}\alpha_1$ and $\text{CuK}\alpha_2$ radiations, that is, with wavelengths of 1.54051 a.u. and 1.54433 a.u., respectively. The lines were indexed and corresponded to $(h^2 + k^2 + l^2)$ values of $48\alpha_1$ and α_2 , $44\alpha_1$ and α_2 , $43\alpha_1$ and α_2 , $40\alpha_1$ and α_2 , $36\alpha_1$ and α_2 , and $35\alpha_1$ and α_2 .

The data supplied to the IBM-704 Computer included the measured angles, their corresponding index number, the wavelength for the line, and a weighting value. The number of lines to be analyzed was included. A starting value of A_0 , which corresponded to $\lambda^2/4a^2$, was supplied to the computer.

The computer calculated the lattice parameter under six separate conditions, listed in the body of this report. The value of the lattice parameters for the different conditions are given in Tables AI through AVI of this Appendix. Also given are the probable errors (P.E._{a_0}) for the parameter and the value of $\sum W_i v_i^2 / (n-k-1) \sum W_i$, which is the σ^2 for the v_i value and which is useful in evaluating the fit of the lattice parameters to the observed data.

It may be observed that there are variations in the values of the lattice parameters when different weighting factors or different systematic corrections are used. The parameter reported in Table I was the one for which the smallest σ^2 value was observed.

Table AI

LATTICE PARAMETERS FOR URANIA-NEODYMIA SOLID SOLUTIONS USING
VARIOUS CORRECTION TERMS AND WEIGHTSSamples Sintered in Combustion Atmosphere at 1650°C for 4 hr and
Parameters Determined Immediately after Sintering

Sample No.	Nominal Sample Composition, m/o Nd ₂ O ₃		Correction Term and Weight					
			AW ¹	AW ²	AD ¹ W ¹	AD ¹ W ²	AE ² W ¹	AE ² W ²
A4N10	10	a ₀ PEa ₀ σ ²	5.43164 0.000068 1.1419 × 10 ⁻⁸	5.43168 0.000030 7.4832 × 10 ⁻⁹	5.43188 0.000140 1.2486 × 10 ⁻⁸	5.43174 0.000049 8.2769 × 10 ⁻⁹	5.43188 0.000130 1.2453 × 10 ⁻⁸	5.43174 0.000046 8.2653 × 10 ⁻⁹
A5N20	20	a ₀ PEa ₀ σ ²	5.40969 0.000972 2.0979 × 10 ⁻⁶	5.41796 0.000459 1.7255 × 10 ⁻⁶	5.43080 0.000114 7.6787 × 10 ⁻⁹	5.43067 0.000036 4.6539 × 10 ⁻⁹	5.42877 0.000145 1.4432 × 10 ⁻⁸	5.42948 0.000051 1.0211 × 10 ⁻⁸
A6N30	30	a ₀ PEa ₀ σ ²	5.41003 0.000950 2.2850 × 10 ⁻⁶	5.42010 0.000495 2.0337 × 10 ⁻⁶	5.43617 0.000151 1.4519 × 10 ⁻⁸	5.43578 0.000052 9.5831 × 10 ⁻⁹	5.43374 0.000162 1.9300 × 10 ⁻⁸	5.43430 0.000055 1.1691 × 10 ⁻⁸
A7N40	40	a ₀ PEa ₀ σ ²	5.44111 0.000070 1.1845 × 10 ⁻⁸	5.44152 0.000039 1.1427 × 10 ⁻⁸	5.44200 0.000131 1.0424 × 10 ⁻⁸	5.44221 0.000054 8.8904 × 10 ⁻⁹	5.44188 0.000122 1.0639 × 10 ⁻⁸	5.44212 0.000052 9.0810 × 10 ⁻⁹
A8N50	50	a ₀ PEa ₀ σ ²	5.42098 0.000937 2.1960 × 10 ⁻⁶	5.43042 0.000513 2.0159 × 10 ⁻⁶	5.44745 0.000136 1.1294 × 10 ⁻⁸	5.44722 0.000050 7.6837 × 10 ⁻⁹	5.44491 0.000149 1.5580 × 10 ⁻⁸	5.44556 0.000059 1.1724 × 10 ⁻⁸
A9N60	60	a ₀ PEa ₀ σ ²	5.42560 0.000878 1.9212 × 10 ⁻⁶	5.43439 0.000492 1.8029 × 10 ⁻⁶	5.45065 0.000096 5.5259 × 10 ⁻⁹	5.45064 0.000041 4.8483 × 10 ⁻⁹	5.44819 0.000139 1.3440 × 10 ⁻⁸	5.44900 0.000061 1.2178 × 10 ⁻⁸
A10N70	70	a ₀ PEa ₀ σ ²	5.46944 0.000164 6.3669 × 10 ⁻⁸	5.47049 0.000102 6.3747 × 10 ⁻⁸	5.47311 0.000245 3.1766 × 10 ⁻⁸	5.47300 0.000130 3.5055 × 10 ⁻⁸	5.47275 0.000223 3.1167 × 10 ⁻⁸	5.47273 0.000120 3.4805 × 10 ⁻⁸

$$\sigma^2 = \frac{\sum Wv^2}{(n-k-1)\sum W}$$

Table AII

LATTICE PARAMETERS FOR URANIA-NEODYMIA SOLID SOLUTIONS USING
VARIOUS CORRECTION TERMS AND WEIGHTSSamples Sintered in Hydrogen Atmosphere at 1650°C for 4 hr
and Parameters Determined Immediately after Sintering

Sample No.	Nominal Sample Composition, m/o Nd ₂ O ₃		Correction Term and Weight					
			AW ¹	AW ²	AD ¹ W ¹	AD ¹ W ²	AE ² W ¹	AE ² W ²
E13N10	10	a ₀ PEa ₀ σ ²	5.46766 0.000133 3.2439 × 10 ⁻⁸	5.46793 0.000092 2.7013 × 10 ⁻⁸	5.47067 0.000343 2.37247 × 10 ⁻⁸	5.47075 0.000222 1.8024 × 10 ⁻⁸	5.47020 0.000300 2.4027 × 10 ⁻⁸	5.47029 0.000193 1.8245 × 10 ⁻⁸
E14N20	20	a ₀ PEa ₀ σ ²	5.46014 0.000529 2.5849 × 10 ⁻⁷	5.46087 0.000416 2.7616 × 10 ⁻⁷	5.46786 0.000909 8.2461 × 10 ⁻⁸	5.46848 0.000709 9.0046 × 10 ⁻⁸	5.46661 0.000835 9.2198 × 10 ⁻⁸	5.46718 0.000646 1.0080 × 10 ⁻⁷
E10N30	30	a ₀ PEa ₀ σ ²	5.44945 0.000095 1.6974 × 10 ⁻⁸	5.44950 0.000064 1.6970 × 10 ⁻⁸	5.45017 0.000290 1.8569 × 10 ⁻⁸	5.44999 0.000193 1.5339 × 10 ⁻⁸	5.45009 0.000253 1.8475 × 10 ⁻⁸	5.44995 0.000167 1.5274 × 10 ⁻⁸
E6N40	40	a ₀ PEa ₀ σ ²	5.45148 0.000120 3.5063 × 10 ⁻⁸	5.45246 0.000071 3.4538 × 10 ⁻⁸	5.45416 0.000167 1.6044 × 10 ⁻⁸	5.45436 0.000071 1.3131 × 10 ⁻⁸	5.45387 0.000156 1.6386 × 10 ⁻⁸	5.45415 0.000068 1.3612 × 10 ⁻⁸
E11N50	50	a ₀ PEa ₀ σ ²	5.44714 0.000125 2.9491 × 10 ⁻⁸	5.44750 0.000096 3.0791 × 10 ⁻⁸	5.45036 0.000277 1.6915 × 10 ⁻⁸	5.45076 0.000197 1.5974 × 10 ⁻⁸	5.44982 0.000248 1.7754 × 10 ⁻⁸	5.45020 0.000176 1.6901 × 10 ⁻⁸
E5N60	60	a ₀ PEa ₀ σ ²	5.45247 0.000484 2.1811 × 10 ⁻⁷	5.45295 0.000350 1.9950 × 10 ⁻⁷	5.45828 0.001189 1.4699 × 10 ⁻⁷	5.45798 0.000888 1.5009 × 10 ⁻⁷	5.45744 0.001033 1.4609 × 10 ⁻⁷	5.45724 0.000762 1.4779 × 10 ⁻⁷
E12N70	70	a ₀ PEa ₀ σ ²	5.52122 0.000222 7.2127 × 10 ⁻⁸	5.52134 0.000168 6.9609 × 10 ⁻⁸	5.52368 0.000776 7.6885 × 10 ⁻⁸	5.52345 0.000614 7.6643 × 10 ⁻⁸	5.52333 0.000654 7.6247 × 10 ⁻⁸	5.52314 0.000515 7.6216 × 10 ⁻⁸
E7N80	80	a ₀ PEa ₀ σ ²	5.52294 0.000283 1.3869 × 10 ⁻⁷	5.52302 0.000214 1.2716 × 10 ⁻⁷	5.52513 0.000977 1.5299 × 10 ⁻⁷	5.52446 0.000734 1.4277 × 10 ⁻⁷	5.52494 0.000835 1.5203 × 10 ⁻⁷	5.52435 0.000623 1.4216 × 10 ⁻⁷

$$\sigma^2 = \frac{\sum Wv^2}{(n-k-1)\sum W}$$

Table AIII

LATTICE PARAMETERS FOR URANIA-NEODYMIA SOLID SOLUTIONS USING
VARIOUS CORRECTION TERMS AND WEIGHTSSamples Sintered in Combustion Atmosphere at 1650°C for 4 hr and Allowed to
Stand in Air for 3 Months Prior to Determining Lattice Parameters

Sample No.	Nominal Sample Composition, m/o Nd ₂ O ₃		Correction Term and Weight					
			AW ¹	AW ²	AD ¹ W ¹	AD ¹ W ²	AE ² W ¹	AE ² W ²
AR4N10	10	a ₀	5.43039	5.43039	5.43089	5.43052	5.43088	5.43056
		PEa ₀	0.000099	0.000071	0.000298	0.000208	0.000262	0.000182
		σ ²	1.9093 × 10 ⁻⁸	1.7821 × 10 ⁻⁸	2.1374 × 10 ⁻⁸	2.0331 × 10 ⁻⁸	2.1254 × 10 ⁻⁸	2.0288 × 10 ⁻⁸
AR5N20	20	a ₀	5.42920	5.42956	5.43038	5.43011	5.43029	5.43007
		PEa ₀	0.000070	0.000030	0.000115	0.000039	0.000106	0.000037
		σ ²	1.2248 × 10 ⁻⁸	7.5826 × 10 ⁻⁹	8.5706 × 10 ⁻⁹	5.5434 × 10 ⁻⁹	8.3181 × 10 ⁻⁹	5.3772 × 10 ⁻⁹
AR6N30	30	a ₀	5.43466	5.43470	5.43501	5.43477	5.43501	5.43478
		PEa ₀	0.000059	0.000024	0.000122	0.000038	0.000112	0.000036
		σ ²	8.7542 × 10 ⁻⁹	4.3878 × 10 ⁻⁹	9.3070 × 10 ⁻⁹	4.8230 × 10 ⁻⁹	9.2188 × 10 ⁻⁹	4.7982 × 10 ⁻⁹
AR7N40	40	a ₀	5.44033	5.44082	5.44164	5.44166	5.44150	5.44157
		PEa ₀	0.000060	0.000032	0.000090	0.000029	0.000076	0.000028
		σ ²	8.8631 × 10 ⁻⁹	7.5093 × 10 ⁻⁹	3.9287 × 10 ⁻⁹	2.6225 × 10 ⁻⁹	4.0699 × 10 ⁻⁹	2.6838 × 10 ⁻⁹
AR8N50	50	a ₀	5.44481	5.44560	5.44704	5.44705	5.44682	5.44690
		PEa ₀	0.000088	0.000049	0.000084	0.000032	0.000078	0.000031
		σ ²	1.8684 × 10 ⁻⁸	1.7001 × 10 ⁻⁸	4.1650 × 10 ⁻⁹	2.9810 × 10 ⁻⁹	4.2088 × 10 ⁻⁹	3.0541 × 10 ⁻⁹
AR9N60	60	a ₀	5.44793	5.44887	5.45055	5.45063	5.45028	5.45044
		PEa ₀	0.000093	0.000055	0.000045	0.000017	0.000043	0.000018
		σ ²	2.1206 × 10 ⁻⁸	2.1005 × 10 ⁻⁸	1.1794 × 10 ⁻⁹	8.0533 × 10 ⁻¹⁰	1.2592 × 10 ⁻⁹	1.0044 × 10 ⁻⁹
AR10N70	70	a ₀	5.47141	5.47154	5.47161	5.47185	5.47159	5.47180
		PEa ₀	0.000108	0.000059	0.000242	0.000109	0.000221	0.000102
		σ ²	2.4375 × 10 ⁻⁸	2.0325 × 10 ⁻⁸	2.7700 × 10 ⁻⁸	2.2573 × 10 ⁻⁸	2.7699 × 10 ⁻⁸	2.2641 × 10 ⁻⁸

$$\sigma^2 = \frac{\sum W_i^2}{(n-k-1) \sum W}$$

Table AIV

LATTICE PARAMETERS FOR URANIA-NEODYMIA SOLID SOLUTIONS USING
VARIOUS CORRECTION TERMS AND WEIGHTSSamples Sintered in Hydrogen Atmosphere at 1650°C for 4 hr and Allowed to
Stand in Air for 3 Months Prior to Determining Lattice Parameters

Sample No.	Nominal Sample Composition, m/o Nd ₂ O ₃		Correction Term and Weight					
			AW ¹	AW ²	AD ¹ W ¹	AD ¹ W ²	AE ² W ¹	AE ² W ²
ER4N05	5	a ₀	5.46798	5.46887	5.47103	5.47095	5.47071	5.47072
		PEa ₀	0.000119	0.000069	0.000143	0.000062	0.000131	0.000058
		σ ²	3.4072 × 10 ⁻⁸	2.9990 × 10 ⁻⁸	1.0899 × 10 ⁻⁸	8.2759 × 10 ⁻⁹	1.0840 × 10 ⁻⁸	8.2132 × 10 ⁻⁹
ER14N20	20	a ₀	5.45688	5.45713	5.45949	5.45961	5.45909	5.45920
		PEa ₀	0.000207	0.000159	0.000477	0.000369	0.000420	0.000323
		σ ²	3.9554 × 10 ⁻⁸	4.0894 × 10 ⁻⁸	2.3394 × 10 ⁻⁸	2.5493 × 10 ⁻⁸	2.3971 × 10 ⁻⁸	2.6182 × 10 ⁻⁸
ER10N30	30	a ₀	5.45088	5.45084	5.45118	5.45082	5.45118	5.45085
		PEa ₀	0.000055	0.000029	0.000117	0.000049	0.000107	0.000046
		σ ²	7.4091 × 10 ⁻⁹	5.8297 × 10 ⁻⁹	7.9495 × 10 ⁻⁹	6.4735 × 10 ⁻⁹	7.8779 × 10 ⁻⁹	6.4774 × 10 ⁻⁹
ER6N40	40	a ₀	5.45119	5.45192	5.45238	5.45325	5.45220	5.45305
		PEa ₀	0.000083	0.000061	0.000155	0.000080	0.000146	0.000078
		σ ²	1.6690 × 10 ⁻⁸	2.6076 × 10 ⁻⁸	1.3950 × 10 ⁻⁸	1.6616 × 10 ⁻⁸	1.4468 × 10 ⁻⁸	1.7771 × 10 ⁻⁸
ER5N60	60	a ₀	5.45433	5.45435	5.45501	5.45470	5.45499	5.45471
		PEa ₀	0.000422	0.000284	0.001533	0.001009	0.001334	0.000872
		σ ²	1.6579 × 10 ⁻⁷	1.3081 × 10 ⁻⁷	2.4623 × 10 ⁻⁷	1.9550 × 10 ⁻⁷	2.4546 × 10 ⁻⁷	1.9516 × 10 ⁻⁷
ER7N80	80	a ₀	5.52411	5.52442	5.52809	5.52843	5.52799	5.52770
		PEa ₀	0.000141	0.000118	0.00369	0.000305	0.000320	0.000263
		σ ²	3.4574 × 10 ⁻⁸	3.8357 × 10 ⁻⁸	2.1541 × 10 ⁻⁸	2.4173 × 10 ⁻⁸	2.2203 × 10 ⁻⁸	2.4943 × 10 ⁻⁸

$$\sigma^2 = \frac{\sum W_i^2}{(n-k-1) \sum W}$$

Table AV

LATTICE PARAMETERS FOR URANIA-NEODYMIA SOLID SOLUTIONS USING
VARIOUS CORRECTION TERMS AND WEIGHTSSamples Sintered in Hydrogen Atmosphere at 1650°C for 4 hr,
Then Resintered in Air at 1400°C for 3 hr

Sample No.	Nominal Sample Composition, m/o Nd ₂ O ₃		Correction Term and Weight					
			AW ¹	AW ²	AD ¹ W ¹	AD ¹ W ²	AE ² W ¹	AE ² W ²
ERA13N10	10	a ₀	5.43489	5.43419	5.43848	5.43804	5.43806	5.43768
		PEa ₀	0.000232	0.000151	0.000639	0.000408	0.000558	0.000353
		σ ²	1.0267 × 10 ⁻⁷	7.9170 × 10 ⁻⁸	9.5177 × 10 ⁻⁸	7.4831 × 10 ⁻⁸	9.3953 × 10 ⁻⁸	7.3900 × 10 ⁻⁸
ERA10N30	30	a ₀	5.43419	5.43280	5.43197	5.43084	5.43229	5.43110
		PEa ₀	0.000187	0.000158	0.000350	0.000231	0.000390	0.000221
		σ ²	8.6342 × 10 ⁻⁸	2.0037 × 10 ⁻⁷	7.8104 × 10 ⁻⁸	1.8676 × 10 ⁻⁷	8.0131 × 10 ⁻⁸	1.8943 × 10 ⁻⁷
ERA11N50	50	a ₀	5.44678	5.44695	5.44718	5.44726	5.44714	5.44722
		PEa ₀	0.000066	0.000035	0.000138	0.000056	0.000127	0.000053
		σ ²	1.0618 × 10 ⁻⁸	8.6298 × 10 ⁻⁹	1.1270 × 10 ⁻⁸	8.8837 × 10 ⁻⁹	1.1276 × 10 ⁻⁸	8.9070 × 10 ⁻⁹

$$\sigma^2 = \frac{\sum Wv^2}{(n-k-1)\sum W}$$

Table AVI

LATTICE PARAMETERS FOR URANIA-NEODYMIA SOLID SOLUTIONS USING
VARIOUS CORRECTION TERMS AND WEIGHTSSamples Sintered in Hydrogen at 1650°C for 4 hr, Allowed to Stand in Air for 3 Months,
Analyzed by DTA to 650°C, after which Parameters were Determined

Sample No.	Nominal Sample Composition, m/o Nd ₂ O ₃		Correction Term and Weight					
			AW ¹	AW ²	AD ¹ W ¹	AD ¹ W ²	AE ² W ¹	AE ² W ²
ED13N10	10	a ₀	5.45227	5.45224	5.45205	5.45194	5.45210	5.45201
		PEa ₀	0.000068	0.000051	0.000213	0.000155	0.000186	0.000134
		σ ²	8.7387 × 10 ⁻⁹	8.6774 × 10 ⁻⁹	9.9068 × 10 ⁻⁹	9.7648 × 10 ⁻⁹	9.9242 × 10 ⁻⁹	9.7869 × 10 ⁻⁹
ED10N30	30	a ₀	5.44697	5.44749	5.44752	5.45130	5.44674	5.45004
		PEa ₀	0.000761	0.000563	0.002375	0.001710	0.002071	0.001484
		σ ²	1.0914 × 10 ⁻⁶	1.0624 × 10 ⁻⁶	1.2468 × 10 ⁻⁶	1.1885 × 10 ⁻⁶	1.2472 × 10 ⁻⁶	1.1981 × 10 ⁻⁶
ED6N40	40	a ₀	5.45191	5.45214	5.45311	5.45264	5.45303	5.45262
		PEa ₀	0.000077	0.000038	0.000139	0.000060	0.000127	0.000055
		σ ²	1.4274 × 10 ⁻⁸	1.0008 × 10 ⁻⁸	1.1241 × 10 ⁻⁸	9.3354 × 10 ⁻⁹	1.0872 × 10 ⁻⁸	9.0892 × 10 ⁻⁹
ED11N50	50	a ₀	5.45163	5.45179	5.45197	5.45207	5.45193	5.45204
		PEa ₀	0.000037	0.000019	0.000075	0.000028	0.000070	0.000026
		σ ²	3.3151 × 10 ⁻⁹	2.3926 × 10 ⁻⁹	3.3085 × 10 ⁻⁹	2.0709 × 10 ⁻⁹	3.3263 × 10 ⁻⁹	2.1016 × 10 ⁻⁹
ED5N60	60	a ₀	5.45382	5.45397	5.45517	5.45536	5.45495	5.45511
		PEa ₀	0.000075	0.000054	0.000206	0.000138	0.000181	0.000120
		σ ²	1.0527 × 10 ⁻⁸	9.5385 × 10 ⁻⁹	9.1418 × 10 ⁻⁹	7.5527 × 10 ⁻⁹	9.2908 × 10 ⁻⁹	7.7211 × 10 ⁻⁹
ED7N80	80	a ₀	5.51883	5.51878	5.51860	5.51827	5.51872	5.51843
		PEa ₀	0.000142	0.000111	0.000522	0.000417	0.000443	0.000352
		σ ²	2.9629 × 10 ⁻⁸	3.0479 × 10 ⁻⁸	3.5466 × 10 ⁻⁸	3.6158 × 10 ⁻⁸	3.5526 × 10 ⁻⁸	3.6290 × 10 ⁻⁸

$$\sigma^2 = \frac{\sum Wv^2}{(n-k-1)\sum W}$$

One of the benefits of the least-squares extrapolation method is the ability to determine if a systematic error exists, to detect its degree, and to aid in the selection of the most suitable systematic correction. By plotting the value of v , which corresponds to the difference between $\sin^2\theta_i$ (computed) and $\sin^2\theta_i$ (observed), against the measured angle, it is possible to observe if a systematic error exists. From the plot one can pick out large deviations in individual observations which indicate errors in θ or incorrect indexing.

Two examples of plotting v against θ are given in Figures 1A and 2A. Figure 1A is the plot for sample A4N10, which was a urania-neodymia solid solution, sintered in air for 4 hr and 1650°C, with a nominal neodymia content of 10 m/o. There is a randomness in the data. The observations fall on both sides of the zero line in no definite pattern. The open circles are the data with no systematic corrections and with all observations weighted equally (AW^1). Plotted, by closed circles, are the data for weighted observations (AW^2), where W^2 is a short notation for $w/\sin^2 2\theta$. The v values

Figure 1A
Variance for Pattern Showing
No Systematic Error

Figure 2A
Variance for Pattern Showing
Systematic Error

are essentially the same at all angles. Although they were not plotted, essentially the same results were obtained with each set of corrections. Here, no systematic error existed and no benefit was derived from applying corrections. The parameter values for A4N10 are given in Table AI. It will be observed that a_0 varied between a value of 5.43164 a.u. for AW^1 and 5.43188 a.u. for AD^1W^1 and AE^2W^1 . The σ^2 values varied between 1.1419×10^{-8} for AW^1 and 8.2653×10^{-9} for AE^2W^2 .

The difference in observed and calculated data for sample A5N20, with a nominal neodymia content of 20 m/o, is plotted in Figure 2A. The open circles correspond to uncorrected data with equal weightings (AW^1). The v values diminish progressively from $+580 \times 10^{-6}$ for a θ value of 80.4° to -658×10^{-6} for a θ value of 57.8° . There is a systematic error in these data. The broken line gives an indication of the change in values. Plotted as closed circles is the AD^1W^2 correction, where D^1 represents a systematic correction of $\sin^2 2\theta$ and W^2 represents a weighting value of $w/\sin^2 2\theta$. It will be observed that the v values are closer, for the most part, to the zero line. The σ^2 value for the AD^1W^2 correction is 4.6539×10^{-9} , the smallest of the values of $\sum Wv^2/(n-k-1)\sum W$.

The v value at 69.4° for the AW^1 determination departs from the curve of systematic error. The value of v for the AD^1W^2 determination is $+704 \times 10^{-6}$ at 69.4° . This deviates markedly from the other data. This indicates that the θ value may be in error or that the value is incorrectly indexed. In this instance, the indexing was correct.

For sample A5N20, the lattice parameter value varied from 5.40969 a.u. for the (AW^1) correction, which is no correction, to 5.43080 a.u. for the (AD^1W^1) correction. The σ^2 value for the (AD^1W^2) correction was 4.6539×10^{-9} ; the a_0 value was 5.43067 a.u. It is interesting to note the large departure of the a_0 value for the (AW^1) and (AW^2) corrections together with the value of σ^2 for these data, which are 2.0979×10^{-6} and 1.7255×10^{-6} , respectively.

It is possible under this program to apply many different correction values and weightings to the raw data. The corrections applied in this study were selected as being the ones most commonly employed. The urania-neodymia solid solutions studied were face-centered cubic of the fluorite type. This program has application to the hexagonal and orthorhombic crystal systems as well.