R. E. Rundle for many helpful discussions and suggestions during the course of this work and to D. T. Hooker for the work on the effect of particle size, suspending medium and mixed crystal formation on the absorption spectra.

AMES, IOWA

Solid Phase Transitions in the UO2–ZrO2 System[1]

BY GERARD M. WOLTEN

RECEIVED FEBRUARY 26, 1958

Several aspects of the UO2–ZrO2 system have been studied and the following conclusions reached: At 2300°, the UO2–ZrO2 system consists of a homogeneous phase extending from 0 to 100 mole % ZrO2. The crystal structure of this phase changes in a continuous manner from cubic for pure UO2 to tetragonal for ZrO2 rich mixtures. At temperatures above 2200°, the structure remained cubic for samples of increasing ZrO2 content until 53–54 mole % ZrO2 was reached, at which point the tetragonal structure was first recognized. The temperature at which pure zirconia transforms from a monoclinic to a tetragonal structure is lowered drastically by additions of urania, to the extent of approximately 100° per mole % UO2 added.

Introduction

A phase diagram for the UO2–ZrO2 system has been reported,[2] but several important aspects of the system are still in doubt or unknown. In this investigation, information was obtained relative to the following three aspects: (1) the effect of UO2 additions on the monoclinic-to-tetragonal transformation temperature of ZrO2, (2) phase relationships in the binary system above 1950°, (3) the probable number of allotropic modifications of zirconia.

Experimental

The effect of urania additions on the monoclinic-to-tetragonal inversion of zirconia was investigated by X-ray diffraction of specimens containing varying amounts of UO2 in a high-temperature Geiger counter diffractometer.[3] The specimens were solid solutions, prepared by sintering the appropriate mixtures at approximately 2000°. The intensity of the monoclinic 111 line was measured as a function of the temperature and interpreted as a measure of the amount of the monoclinic phase present.

In order to investigate the phase relationships above 2000°, mixtures of UO2 and ZrO2 of known composition were compressed into high-density tablets and heated under a reduced pressure of argon to 2300 ± 100° for 2 hr. They were then quenched to room temperature. The furnace and quenching apparatus are described elsewhere.[4] Since at these high temperatures, the vapor pressure of UO2 is of the order of a micron,[5] the surfaces of the specimens lost considerable amounts of UO2. Although the resulting concentration gradients appeared to be large only in the outer layers of the specimens, a successful effort was made to suppress the loss of UO2 by wrapping the tablets tightly in tantalum foil. This resulted in homogeneous specimens which were suitable for bulk chemical analysis, so that a reliable correlation between composition and lattice parameters could be obtained.

Results and Discussion

On crystallographic grounds, urania would be expected to be more soluble in the tetragonal form of zirconia than in the monoclinic form and hence should lower the transformation temperature. This was found to be the case. The effect is very drastic and comparable in magnitude to that caused by yttria.[6]

The monoclinic-to-tetragonal transformation for 100% ZrO2 has been reported[7,8] to occur over a range of temperatures and to exhibit hysteresis. This was found to be the case also for the compositions examined in this work, but the X-ray method permitted the beginning of the forward transformation on heating to be clearly recognized. A typical plot of intensity vs. temperature is shown in Fig. 1, for a sample containing 5 mole % UO2. The intensity of the 111 line remained constant up to a certain temperature and then declined linearly with further increases in temperature; while simultaneously, the tetragonal pattern appeared and became more intense. The sharp break in the plot of the monoclinic 111 line intensity vs. the temperature was taken as the beginning of the transformation under the conditions of the experiment, and the corresponding temperatures for several different compositions are listed in Table I.

TABLE I

TEMPERATURE OF INCIPIENT MONOCLINIC-TO-TETRAGONAL TRANSFORMATION AS A FUNCTION OF COMPOSITION

Mole % UO2	Temp., °C.
0 (pure ZrO2)	1100 [7]
2	910
5	540
10	~0[a]
15	≪0[b]

[a] Both phases present at room temperature. [b] Specimen entirely tetragonal at room temperature.

In the investigation of binary phase relationships above 2000°, it was found that none of the samples showed the presence of more than one phase, although urania has a cubic crystal structure (fluorite type), while the high temperature form of zirconia is tetragonal (slightly distorted fluorite structure of axial ratio 1.018).

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) W. A. Lambertson and M. H. Mueller, J. Am. Ceram. Soc., 36, 365 (1953).

(3) P. Chiotti, Rev. Sci. Instr., 25, 683 (1954).

(4) S. B. Austerman, G. M. Wolten and C. T. Broman "A High-Temperature Vacuum Quench Furnace," NAA-SR-2312, 1958.

(5) R. J. Ackerman, "The High-Temperature, High-Vacuum Vaporization and the Thermodynamic Properties of Uranium Dioxide," ANL-5482, 1955, p. 82.

(6) P. Duwez, F. H. Brown, Jr., and F. Odell, J. Electrochem. Soc., 98, 356 (1951).

(7) P. Murray and E. B. Allison, Trans. Brit. Ceram. Soc., 53, 335 (1954).

(8) A. Dietzel and H. Tober, Ber. deut. keram. Ges., 30, 47 (1953).

Lattice parameters for the various compositions generally were calculated from the 004/400 lines. Where the back reflections were not sharp, there was some scatter in the values, and only those were accepted for which several determinations agreed. The results are listed in Table II and plotted in Fig. 2, where they are also compared with those of other investigators.[2] A continuous solid solution is indicated by the absence of a discontinuity in the plot of the lattice parameters vs. composition, as well as the absence of two-phase specimens.

TABLE II

STRUCTURES AND LATTICE PARAMETERS OF SPECIMENS QUENCHED FROM 2300°

Mole % ZrO_2	Structure	a_0, A.	c_0
0	Cubic	5.469	
49.81	c	5.304	
52.0	c	5.307	
52.5	c	5.30	
53.0	c	5.299	
53.5	c	5.296	
54.6	Tetragonal	5.28	5.29
55.0	Doubtful, either cubic or tetragonal	5.284	a
56.0	Tetragonal	5.281	5.290
60.6	t	5.25	5.28
62.0	t	5.24	5.28
72[b]	t	5.210	5.268
76	t	5.19	5.27
100.0	t	5.07	5.16 (ref. 9)

a The value 5.284 is probably the average of a_0 and c_0 for this composition. b This composition was not determined by analysis but inferred from the value of a_0.

This work agrees with that of the previous investigators with respect to the continuity of the lattice parameters and the non-observance of two-phase samples. There are, however, some disagreements between the respective numerical values of the lattice parameters. These can be explained as follows:

It seems likely that the UO_2 used by the other workers contained oxygen in excess of the stoichiometric value, since the reported lattice constant would correspond to the composition $UO_{2.12}$.[10] The urania used in this work had the composition $UO_{2.00}$. An oxygen content in excess of the stoichiometric value is believed[11] to give rise to a very appreciable vapor pressure of UO_3, in addition to the normal vapor pressure of UO_2. The loss of uranium and the resulting concentration gradients would thus be appreciable. One may be inclined, therefore, to credit the lattice parameter and concentration measurements reported in this paper with a slightly higher degree of accuracy, because of the precautions taken to avoid concentration gradients.

While the presence of a continuous solid solution at high temperatures appears well established by the foregoing, it may be that the tetragonal crystal structure of the higher-zirconia content specimens is due to a transformation not suppressed by the quenching. If there existed a high temperature

(9) O. Ruff and F. Ebert, Z. anorg. allgem. Chem., **180**, 19 (1929).
(10) S. M. Lang, et al., "High-Temperature Reactions of Uranium Dioxide with Various Metal Oxides," NBS Circular 568, 1956, p. 3.
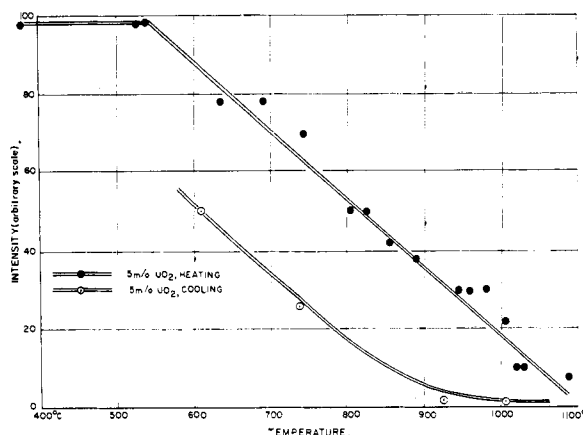(11) L. Brewer, Chem. Revs., **52**, 54 (1953).

Fig. 1.—Intensity of monoclinic 111 diffraction line in ZrO_2–UO_2 mixtures vs. temperature.

cubic form of zirconia, then the UO_2–ZrO_2 solid solution would be cubic at all concentrations, and the tetragonal structure would arise from a fast, diffusionless transformation during quenching, as in the Cu–Mn system.[12,13] A high temperature cubic form of zirconia never has been observed, although a report of a hexagonal form[14,15] has been misquoted[16] to the effect that there is a cubic form. Furthermore, the contents of the report concerning this hexagonal modification never has been confirmed. While there is thus no reliable evidence for an additional high temperature form of zirconia, the occurrence of a transformation in the solid solutions would constitute such evidence and, furthermore, would lead to the conclusion that this high temperature form is cubic.

Two techniques were used to search for such a transformation: observations of the changing X-ray pattern while the specimen goes through the transformation temperature and examination of the microstructure of the quenched specimens.

Assuming that the transformation occurs, it should occur above 1800° for 100% zirconia since it is known that ZrO_2 remains tetragonal up to this temperature.[9] Also, since specimens with less than 53 mole % ZrO_2 remained cubic when quenched to room temperature, a transformation temperature of about 20° might be taken for this composition. Extrapolating these data, it is estimated that cooling to the temperature of liquid nitrogen should be sufficient to bring about a cubic-to-tetragonal transformation in a sample containing 50 mole % ZrO_2. Even at this low temperature, the transformation would be expected to be almost instantaneous, again by analogy with the Cu–Mn system and martensite reactions generally. However, on scanning the X-ray pattern of a 50% specimen immersed in liquid nitrogen, no change in crystal structure was observed.

As a further test, the tetragonal phase, if it re-

(12) Z. S. Basinski and J. W. Christian, J. Inst. Metals, **1**, 659 (1952).
(13) U. Zwicker, Z. Metallkunde, **42**, 327 (1951).
(14) W. M. Cohn and S. Tolksdorf, Z. physik. Chem., **B8**, 331 (1930).
(15) W. M. Cohn, Trans. Electrochem. Soc., **68**, 65 (1935).
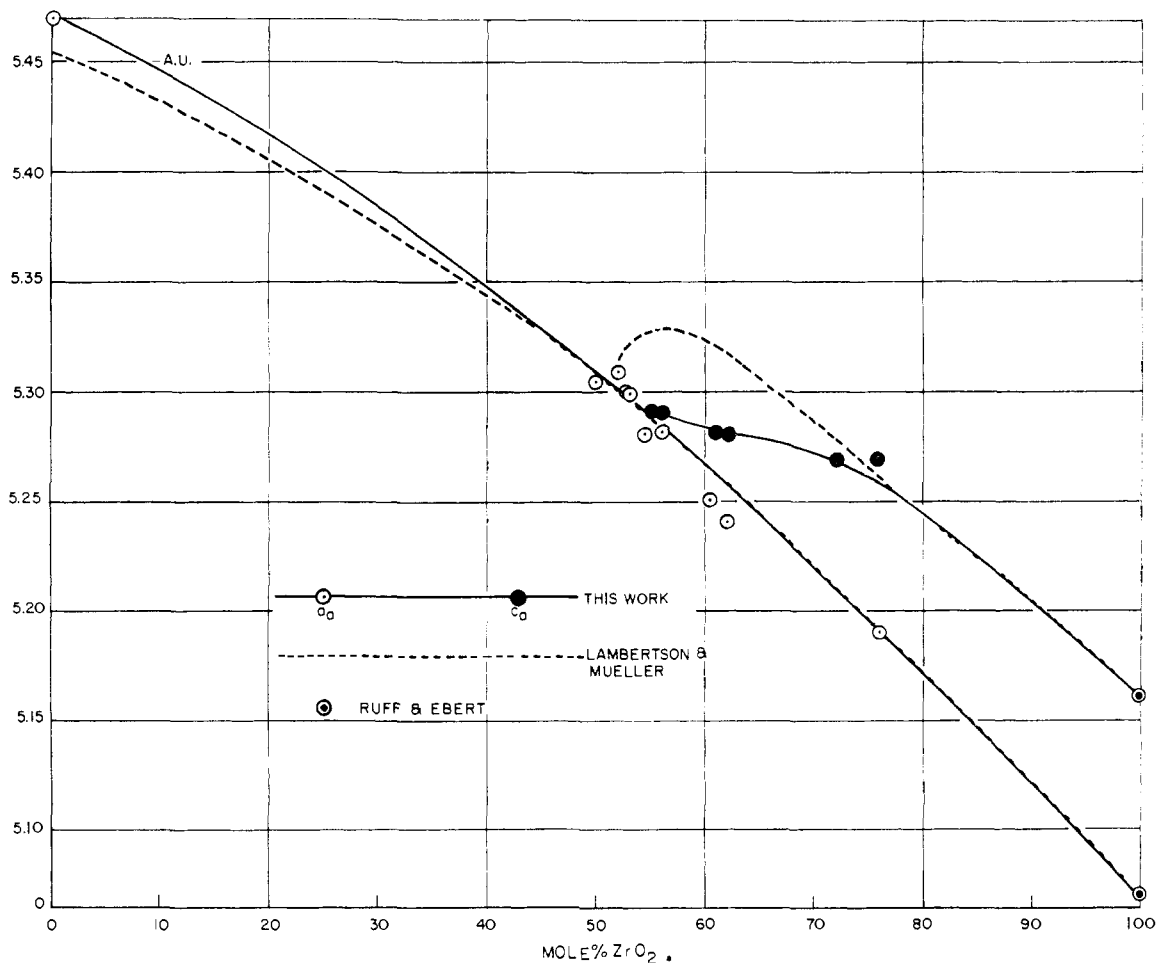(16) H. G. Sowman and A. J. Andrews, J. Am. Ceram. Soc., **34**, 298 (1951).

Fig. 2.—Lattice parameters of UO_2-ZrO_2 solid solutions quenched from 2300°.

sulted from a cubic phase by a diffusionless transformation, should also exhibit an extensively twinned microstructure, recognizable under polarized light by banded grains. This was observed in both the Cu–Mn and the In–Tl systems.[17] Several of the tetragonal quenched UO_2-ZrO_2 specimens were polished, etched and examined with a polarizing microscope. The grains were smooth and gave no indication of a banded structure. From these tests, it would appear that no transformation had occurred during quenching.

General Discussion

A revised phase diagram for the UO_2-ZrO_2 system is shown in Fig. 3. Its principal new features are a continuous solid solution above 1950° and the boundaries between the tetragonal and monoclinic phases. The lower boundary, shown as a solid line, defines the experimentally observed beginning of the transformation on heating. The upper, dashed boundary, marking the completion of the transformation on heating, is placed arbitrarily except for the composition 100% ZrO_2.[7] These lines are not necessarily to be interpreted as conventional equilibrium curves, because a preponderance of the published information concerning the

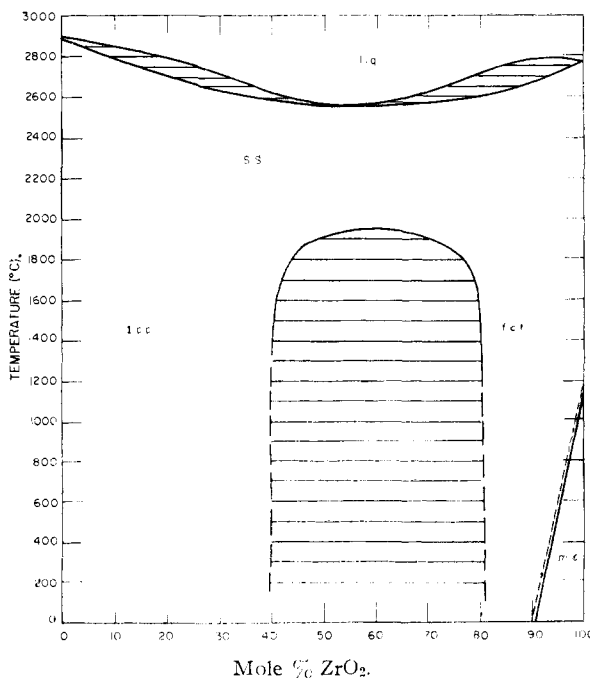(17) J. S. Bowles, C. S. Barrett and L. Guttman, J. Metals, Trans. AIME, 188, 1478 (1950).

Fig. 3.—Revised phase diagram for the system UO_2-ZrO_2.

monoclinic-to-tetragonal transformation of ZrO_2,[7,8] as well as the behavior of ZrO_2-rich specimens observed in this work, suggest that the kinetics of the transformation are martensitic.

Some comments are also in order concerning the high temperature continuous solid solution between cubic UO_2 and tetragonal ZrO_2. It is usually considered necessary for the existence of a continuous solid solution that the components have the same crystal structure. However, this does not necessarily mean identity of the crystallographic system but rather sufficient similarity of the atomic arrangements to permit random substitution. Both UO_2 and ZrO_2 have a fluorite-type structure, which in the latter case is very slightly distorted to give a tetragonal axial ratio of 1.018. Urania, being cubic, has an axial ratio of 1.000. Obviously, there is very little difference between the two structures, and since the ionic radius of U(IV) is only 12% larger than that of Zr(IV), a continuous solid solution is a reasonable expectation. This phenomenon has been observed in several other systems, listed in Table III. In all these systems, the components, although belonging to different crystallographic systems, form continuous solid solutions. However, where the structures are known in sufficient detail, it is apparent that the lattice of one component is quite similar to that of the other, a phenomenon which one might call hidden or krypto-isomorphism.

Acknowledgments.—The author is indebted to Professor J. E. Ricci for valuable criticism of a

preliminary report, to Mr. S. B. Austerman for suggesting the project and giving it much valuable guidance and support, to Dr. R. Chang for drawing attention to the martensitic behavior of the zirconia

TABLE III

PAIRS OF NON-ISOMORPHOUS COMPOUNDS WHICH FORM CONTINUOUS SOLID SOLUTIONS

Compd.	Lattice types	Ref.	Compd.	Lattice types	Ref.
LiCl	FCC	18	Fe₃O₄	FCC	23
MgCl₂	Rhombohedral	19	Mn₃O₄	BC tetragonal	
LiCl	FCC	20	UO₂	FCC (fluorite str.)	This work
FeCl₂	Rhombohedral		ZrO₂	FC tetragonal (distorted fluorite structure)	
LiF	FCC				
MgF₂	BC tetragonal (rutile struct.)				
UC	FCC	21	U₃O₈	Orthorhombic	24
UC₂	FC tetragonal	22	UO₃	Hexagonal	

transformation and to Messrs. T. C. Broman and V. Robling for their able assistance with many of the experiments.

(18) C. Sandonnini, Atti reale Accad. Lincei, [5] **22**, 629 (1913).

(19) G. Bruni and A. Ferrari, Z. Krist., **89**, 499 (1934).

(20) C. Beusman, "Activities in the KCl–FeCl₂ and LiCl–FeCl₂ Systems," ORNL-2323, 1957.

(21) A. G. Bergman and E. P. Dergunov, Compt. rend. Acad. Sci. USSR., **31**, 755 (1941).

(22) M. W. Mallett, A. F. Gerds and H. R. Nelson, J. Electrochem. Soc., **99**, 197 (1952).

(23) H. V. Eckerman, Geol. Förhandl., **65**, 258 (1943).

(24) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium Compounds," Part I, McGraw–Hill Book Co., Inc., New York, N. Y., 1951, p. 256.

CANOGA PARK, CALIF.

# Addition Compounds of Metal Halides with POX₃ Compounds

BY J. C. SHELDON AND S. Y. TYREE

The P–O band in the infrared spectra of solid addition compounds between phosphoryl halides and metal halides is shown to shift to a lower frequency with respect to the pure phosphoryl halide. The shift is interpreted as suggesting that the bonding in the addition compounds is through oxygen. Triphenylphosphine oxide–metal halide addition compounds have been synthesized as models for comparison in which the bonding can be only through oxygen. Phase studies are reported for the systems TiBr₄–PBr₃, POBr₃–SnBr₄, POCl₃–SnCl₄.

In recent years a series of crystalline addition compounds of phosphoryl halides with anhydrous metal halides has been reported, notably by Gutmann.[1] The bonding has been regarded as due to halogen-bridge formation, using one of the halogen atoms in the phosphorus compound. Whether or not the crystalline addition compounds are regarded as covalent, it also has been postulated that the compounds ionize upon melting or upon dissolution in polar solvents,[1,2] cf. equation 1

$$POCl_3 \cdot AlCl_3 \rightleftharpoons POCl_2^+ AlCl_4^-$$ (1)
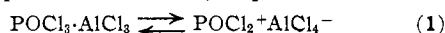
It is true that the acid character of polyvalent metal halides in phosphoryl halide solvents[3] may be adequately explained by the solvo theory of acids and bases. The only direct evidence on structures of such compounds is the Raman spectrum of solid

$POCl_3 \cdot SbCl_5$,[4] which is interpreted to indicate the presence of $SbCl_6^-$ ions in the crystal. No X-ray structure determinations have been made on any of the compounds. Transport measurements and conductivity studies of the compounds, either in the liquid state or as solutes, have been offered as support for the ionic structures.[5,6] It is quite possible that small amounts of ions of the types POX_2^+ and $MeCl_{n+1}^-$ do exist in solutions of the addition compounds, while the crystalline addition compounds may be of essentially different structure types.

The P–O bond order in compounds of the type $X_2P{=}O^+ MeX_{n+1}^-$ would be greater than that in compounds of the type $X_3\overset{+}{P}-{>}\overset{-}{O}$, which in turn

(1) V. Gutmann, Z. anorg. allgem. Chem., **269**, 279 (1952).

(2) N. N. Greenwood and K. Wade, J. Chem. Soc., 1516 (1957).

(3) J. P. McReynolds, J. Chem. Educ., **17**, 116 (1940).

(4) A. Maschka, V. Gutmann and R. Sponer, Monatsh., **86**, 52 (1955).

(5) V. Gutmann and R. Himml, Z. physik. Chem. N. F., **4**, 157 (1955).

(6) V. Gutmann, Z. anorg. allgem. Chem., **270**, 179 (1952).