JOURNAL OF SOLID STATE CHEMISTRY 4, 324–330 (1972)

The Rhenium–Oxygen System at High Pressure: Structure and Characterization of a New Rhenium Oxide

W. JEITSCHKO AND A. W. SLEIGHT

Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

Received June 25, 1971

The rhenium–oxygen system has been studied under 65 kbar pressure. In addition to the known ReO_2, ReO_3, and Re_2O_7 phases, a new, nonstoichiometric phase has been found. This phase can be represented as $Re_{1+x}O_3$ where values of x from 0.14 to 0.21 have been observed. The structure of this new phase has been determined for $x = 0.16$. The space group is $P6_322$, and the hexagonal cell dimensions are $a = 4.8350 \pm 0.0006$ Å and $c = 4.5350 \pm 0.001$ Å. The structure is based on hexagonally close-packed oxygens with rheniums in certain of the octahedral sites. Crystals of this new rhenium oxide show metallic conductivity. The relation of the $Re_{1+x}O_3$ structure to other structures with hexagonal close-packed anions is discussed.

Introduction

In mixed oxides rhenium has been found in all oxidation states from 3+ to 7+, e.g., $NaRe^{7+}O_4$, $Ba_2MgRe^{6+}O_6$ (*1*), $Cd_2Re_2^{5+}O_7$ (*2*), $Na_2Re^{4+}O_3$ (*3*), and $LiRe^{3+}O_2$ (*3*). Compounds where rhenium formally has a fractional oxidation state are also known, e.g., $La_4Re_6^{4.3+}O_{19}$ (*4*, *5*), $Na_{0.9}Re^{5.1+}O_3$ (*6*), and $K_{0.3}Re^{5.7+}O_3$ (*6*). However, in the binary Re–O system only the 7+, 6+, and 4+ oxidation states have been found, i.e., Re_2O_7, ReO_3, and two forms of ReO_2 (*7*). We examined the Re–O system at high pressure, and a new nonstoichiometric oxide of rhenium was found (*8*).

Synthesis

Rhenium trioxide was prepared from Re_2O_7 by the *p*-dioxane method (*9*). The ReO_3 produced was washed with water and then dried to remove any traces of Re_2O_7. The ReO_2 was prepared by the reaction of Re and ReO_3 in silica ampoules. All high-pressure experiments were conducted in a tetrahedral anvil which has been previously described (*10*). The containers were either gold or platinum, and the products were quenched to room temperature under pressure.

Mixtures of Re_2O_7–ReO_3, ReO_3–ReO_2, and ReO_2–Re were heated at 700–1400°C under 65 kbar pressure. The only new phase found was formed from the ReO_3–ReO_2 mixture. It is copper–gold colored and distinctly different in appearance from red ReO_3 and black ReO_2.

Characterization

X-Ray powder patterns were obtained at 25°C using a Hägg–Guinier camera with $CuK\alpha_1$ radiation and an internal standard of high-purity KCl ($a = 6.29310$ Å at 25°C). The lattice constants were refined by the least-squares method. The powder pattern of the new phase was simple and readily indexed as hexagonal. The cell dimensions varied from $a = 4.8362 \pm 0.0002$ Å and $c = 4.5197 \pm 0.0003$ Å ($c/a = 0.9346$ and $V = 91.55 \pm 0.01$ Å^3), to $a = 4.8194 \pm 0.0003$ Å and $c = 4.5825 \pm 0.0004$ Å ($c/a = 0.9508$ and $V = 92.18 \pm 0.01$ Å^3). The larger volume was found when ReO_2 was present as a second phase; the smaller when ReO_3 was present. Note that as the *c*-axis and volume increase, the *a*-axis decreases.

Chemical analyses were carried out both by tga hydrogen reduction and by an inert gas fusion method (*11*). With the formula represented as $Re_{1+x}O_3$, x is found to be 0.14 ± 0.01 for the smaller volume limit and 0.21 ± 0.01 for the larger volume limit. Both analytical procedures agreed well within the error limits given.

We considered the possibility that the hexagonal phase might be impurity stabilized by the inadvertent introduction of a third component, but emission spectroscopic analyses showed no metal other than rhenium. It still seemed possible that hydrogen might be present, i.e., as H_yReO_x or $ReO_x(OH)_y$. Wilhelmi (*12*) found that when MoO_x and WO_x ($2 < x < 3$) are prepared at high pressure in a similar apparatus, hydrogen is incorporated as a third component giving hydroxyoxides. A potential hydrogen source is pyrophyllite, which is used as a pressure transmitting medium. Even if the container is sealed, hydrogen from the water could diffuse through the container walls. Since gold is relatively impervious to hydrogen in contrast to platinum, we used gold containers that were welded closed. Such precautions to exclude water and hydrogen did not prevent the formation of the hexagonal phase. As an additional check, an ir spectrum of the hexagonal phase showed no evidence of water or hydroxyl groups. It, therefore, seems highly probable that the hexagonal phase is a true binary compound of rhenium and oxygen.

The properties of the new hexagonal rhenium oxide are much like those of ReO_2 and ReO_3. Nonoxidizing acids do not attack these compounds, and all are metallicly conducting. Resistivities of the hexagonal phase were measured on crystals of unknown orientation by the four-probe method from 4.2 to 298°K. They varied somewhat from sample to sample but were about $1 \times 10^{-4}\ \Omega$ cm at 4.2°K and gradually increased to about $6 \times 10^{-4}\ \Omega$ cm at room temperature. Somewhat lower resistivities have been reported for ReO_3 (*8*, *13*) and β-ReO_2 (*14*).

Structure Determination

The crystals used for the single crystal X-ray work were grown under pressure with $NaReO_4$ as a flux. The matrix was dissolved with hydrochloric acid and the residue identified as the new oxide and ReO_2. A flame photometry analysis of the product showed only a trace of Na (less than 0.05 wt %). The lattice constants were $a = 4.8350 \pm 0.0006$ Å, $c = 4.5350 \pm 0.0010$ Å, $c/a = 0.9379$, and $V = 91.81 \pm 0.25$ Å^3. Assuming linear dependence of c/a on composition, the formula of the crystals used for the structure determination corresponds to about $Re_{1.16}O_3$.

The single crystals were examined with Mo$K\alpha$ radiation on a Buerger precession camera. The relatively small size of the unit cell and the fact that the composition of the phase varied somewhat as synthesis conditions changed suggested the possible formation of superstructures as known, for example, for the series of phases MoO_{3-x} and WO_{3-x} (*15*). However, superstructure reflections could not be detected on even strongly overexposed precession photographs. The possible occurrence of superstructures in slow-cooled, or low-temperature annealed, high-pressure samples was not investigated.

The diffraction patterns have Laue symmetry $6/mmm$ and reflections $00l$ with $l = 2n + 1$ absent even on overexposed photographs; thus, the space group is uniquely $P6_322$–D_6^6. In addition, reflections $h0l$ with $l = 2n + 1$ and $h = 3n$ are missing. These nonspace-group extinctions result from the combination of high symmetry point positions occupied in the final structure.

The crystal used to collect intensity data was an almost perfect hexagonal prism with an average diameter of about 32 μ and a height of 50 μ. It was mounted with the c direction close to the ϕ axis of a Picker automatic diffractometer (Zr-filtered Mo radiation, scintillation counter with pulse height discriminator). The θ–2θ scan technique was used with a scan speed of 1/2°/min, a scan angle of 2° plus the angular separation of the $K\alpha$ doublet, and a background count of 20 sec.

Two-sixths of all possible reflections within $2\theta = 90°$ were recorded (all reflections with indices all positive or all negative). Reflections hkl and $\overline{khl}$ (even those with weak intensity) were equal within the limits of error, confirming Laue symmetry $6/mmm$. These data were averaged in the final steps of the structure refinement. An absorption correction was made assuming cylindrical crystal shape (*16*).

A structure proposal for an idealized composition ReO_3 was readily worked out on the basis of a qualitative interpretation of the intensity data and geometric considerations. It consists of a hexagonal close-packed arrangement of oxygen atoms with Re in one-third of the available octahedral voids (Table I, proposal 1).

A least-squares refinement of this trial structure was carried out using a full-matrix, least-squares program by Finger (*17*). Atomic scattering factors for the neutral atoms were taken from Cromer and Mann (*18*). The correction for anomalous dispersion of Re was computed with the values of Cromer (*19*). The function minimized was $\Sigma w_i(F_o - KF_c)_i^2$ where w_i is the weight based on counting statistics and K a scale factor. An extinction correction was applied in the form of $F_{\mathrm{corr}}^2 = F_{\mathrm{obs}}^2(1 + CI_{\mathrm{obs}})$, where C is the extinction correction parameter. Reflections with extinction corrections more than 25 % were assigned

TABLE I

RESULTS OF LEAST SQUARES REFINEMENTS OF THE HIGH PRESSURE PHASE $Re_{1+x}O_3$. Parameters listed without standard deviations were held constant during refinement. Proposal No. 5 gives the final parameters. For details see text.

Proposal no.		1	2	3	4	5
Oxygen in *6g* x00	occup.	1	1.12 ± 0.16	1	1	1
	x	0.364 ± 0.007	0.365 ± 0.007	0.361 ± 0.007	0.359 ± 0.002	0.359 ± 0.002
	B(Å^2)	0.79 ± 0.32	1.06 ± 0.48	0.89 ± 0.35	1.16 ± 0.10	0.92 ± 0.08
Rhenium in *2d* $\frac{1}{3}\frac{2}{3}\frac{3}{4}$	occup.	1	1	1	0.90 ± 0.02	1
	B(Å^2)	0.72 ± 0.05	0.72 ± 0.05	0.72 ± 0.05	0.70	0.70 ± 0.02
Rhenium in *2c* $\frac{1}{3}\frac{2}{3}\frac{1}{4}$	occup.	0	0	−0.04 ± 0.01	0	0
	B(Å^2)			0.72		
Rhenium in *2b* 00$\frac{1}{4}$	occup.	0	0	0	0.11 ± 0.01	0.13 ± 0.01
	B(Å^2)				0.70	0.70 ± 0.10
extinction correction parameter (×10^4)		0.29	0.29	0.29	0.29	0.29 ± 0.06
scale factor		1.10 ± 0.03	1.09 ± 0.03	1.10 ± 0.03	1.21 ± 0.03	1.11 ± 0.02
R* (181 observed reflections).		0.13	0.13	0.12	0.03	0.024
R (total of 240 reflections).		0.14	0.14	0.14	0.04	0.043

*$R = \sum \, |F_{obs} - |F_{calc}|| / \sum F_{obs}$.

zero weight in the least-squares cycles and are marked with an asterisk in the list of observed and calculated structure factors (Table II).

To account for the deviations from ideal ReO_3 composition, two basically different proposals were considered:

(1) ReO_{3-x}: a defect in oxygen sites. Refinement of this proposal resulted in a relatively high R-value (Table I, proposal 2). This proposal is also intuitively unreasonable since oxygen atoms should be close-packed for a high-pressure phase.

(2) $Re_{1+x}O_3$: The occupancy of additional interstitial sites by Re atoms. In the idealized proposal ReO_3 only the octahedral sites *2d* $\frac{2}{3}\frac{1}{3}\frac{1}{4}$ were used. Additional octahedral sites are at *2c* $\frac{1}{3}\frac{2}{3}\frac{1}{4}$ and *2b* 00$\frac{1}{4}$. More than twenty combinations of occupancies of these sites and of other variables (thermal parameters, extinction correction, and scale factor) have been studied in least-squares refinements. After a satisfactory structure was obtained, several least-squares refinements were carried out to illustrate the major possible proposals. These results are summarized in Table I. It can be seen that proposals 4 and 5, which permit occupancy of the *2b* site with Re, resulted in a substantial decrease of the R value. Proposal 4 can be ruled out since it is in poor agreement with the composition found by chemical analysis. Proposal 5 which corresponds to a composition $Re_{1.13}O_3$ is considered to give the correct structure. Its composition is close to the expected composition $Re_{1.16}O_3$ mentioned above.

Discussion

The volume per formula unit $Re_{1.16}O_3$ is 45.9 Å^3 as compared to 52.6 Å^3 for the ambient-pressure phase ReO_3. In Table III interatomic distances for the two structures are compared. It can be seen that the closest rhenium–oxygen and oxygen–oxygen distances are the same or longer in the high-pressure phase, as would be expected since $Re_{1.16}O_3$ formally contains about half Re^{5+}, which is larger than Re^{6+}. The higher density of the high-pressure phase is therefore due to the higher efficiency in space filling. In the high-pressure phase oxygen atoms are close-packed with twelve nearest oxygen neighbors. The ambient pressure phase, on the other hand, can be derived from a cubic close-packed oxygen arrangement with one-third of the oxygen positions unfilled, giving only eight close oxygen neighbors.

In both structures the rhenium atoms are surrounded by six oxygen atoms forming an octahedron. All available octahedral interstices are filled with rhenium atoms in the ambient-pressure phase ReO_3. Only one-third of the available octahedral sites are filled fully in the high-pressure phase; another third is partially filled. It can be assumed that the partial filling of this site (*2b*) accounts for the above

TABLE II

Observed and Calculated Structure Factors of the High Pressure Phase $Re_{1.16}O_3$. Reading from left to right, the column contain the values h, k, l, F_{obs}, F_{calc}

1	0	0	57	54•	3	5	1	32	31	3	2	3	49	50	4	1	5	0	3•
2	0	0	37	37	4	5	1	27	25	4	2	3	40	41	5	1	5	29	29
3	0	0	120	122•	1	6	1	36	36	5	2	3	0	3•	6	1	5	24	23
4	0	0	30	31	2	6	1	31	29	6	2	3	26	26	1	2	5	49	49
5	0	0	17	18	3	6	1	0	0•	1	3	3	59	57	2	2	5	4	5•
6	0	0	56	58	1	7	1	0	1•	2	3	3	50	50	3	2	5	37	38
7	0	0	12	15•	0	0	2	117	102•	3	3	3	6	0•	4	2	5	33	32
8	0	0	7	7•	1	0	2	38	39	4	3	3	34	34	5	2	5	3	2•
1	1	0	154	119•	2	0	2	41	41	5	3	3	26	27	1	3	5	42	43
2	1	0	38	37	3	0	2	80	81	1	4	3	6	5•	2	3	5	37	37
3	1	0	34	33	4	0	2	23	23	2	4	3	42	42	3	3	5	0	0•
4	1	0	70	71	5	0	2	25	24	3	4	3	35	35	4	3	5	28	27
5	1	0	19	19	6	0	2	45	46	4	4	3	0	2•	1	4	5	7	3•
6	1	0	17	17	7	0	2	11	11	1	5	3	37	38	2	4	5	31	31
7	1	0	36	34	1	1	2	152	127•	2	5	3	0	3•	3	4	5	27	26
2	2	0	91	89	2	1	2	34	33	3	5	3	27	27	1	5	5	30	30
3	2	0	22	22	3	1	2	27	25	1	6	3	30	30	2	5	5	5	2•
4	2	0	22	22	4	1	2	71	72	2	6	3	27	26	1	6	5	25	24
5	2	0	49	48	5	1	2	17	18	1	7	3	0	1•	0	0	6	52	53
6	2	0	9	11•	6	1	2	12	12	0	0	4	109	104	1	0	6	18	18
3	3	0	71	71	7	1	2	35	34	1	0	4	30	30	2	0	6	18	19
4	3	0	19	19	1	2	2	34	33	2	0	4	24	25	3	0	6	43	44
5	3	0	10	10•	2	2	2	93	92	3	0	4	79	80	4	0	6	12	13
6	3	0	34	34	3	2	2	27	27	4	0	4	20	22	5	0	6	13	14
4	4	0	41	40	4	2	2	19	18	5	0	4	13	13	1	1	6	58	59
5	4	0	11	11•	5	2	2	48	48	6	0	4	43	44	2	1	6	17	17
1	0	1	129	110•	6	2	2	12	13	7	0	4	8	11•	3	1	6	14	14
2	0	1	93	95•	1	3	2	25	25	1	1	4	79	78	4	1	6	41	41
3	0	1	0	0•	2	3	2	27	27	2	1	4	26	25	5	1	6	10	11•
4	0	1	61	64	3	3	2	54	55	3	1	4	22	23	1	2	6	16	17
5	0	1	49	51	4	3	2	15	14	4	1	4	52	52	2	2	6	48	49
6	0	1	0	0•	5	3	2	13	15	5	1	4	15	14	3	2	6	15	15
7	0	1	31	31	1	4	2	71	72	6	1	4	13	13	4	2	6	10	10•
8	0	1	22	24	2	4	2	17	18	1	2	4	25	25	1	3	6	15	14
1	1	1	26	24	3	4	2	16	14	2	2	4	62	63	2	3	6	14	15
2	1	1	87	84	4	4	2	42	41	3	2	4	16	17	3	3	6	33	32
3	1	1	70	69	5	4	2	10	9•	4	2	4	19	16	1	4	6	40	41
4	1	1	7	6•	1	5	2	18	18	5	2	4	39	37	2	4	6	12	10
5	1	1	44	44	2	5	2	49	48	1	3	4	23	23	1	5	6	8	11•
6	1	1	33	34	3	5	2	16	15	2	3	4	15	17	1	0	7	34	36
7	1	1	0	1•	4	5	2	9	9•	3	3	4	53	53	2	0	7	33	34
1	2	1	87	85	1	6	2	12	12•	4	3	4	13	14	3	0	7	5	0•
2	2	1	11	11	2	6	2	12	13	5	3	4	10	8•	4	0	7	26	27
3	2	1	59	59	1	7	2	36	34	1	4	4	50	52	1	1	7	6	4•
4	2	1	47	49	1	0	3	81	82	2	4	4	16	16	2	1	7	31	32
5	2	1	2	3•	2	0	3	73	74	3	4	4	13	14	3	1	7	28	29
6	2	1	30	29	3	0	3	5	0•	4	4	4	32	31	4	1	7	2	2•
1	3	1	71	70	4	0	3	53	54	1	5	4	14	14	1	2	7	32	31
2	3	1	58	59	5	0	3	42	44	2	5	4	39	37	2	2	7	8	3•
3	3	1	6	0•	6	0	3	2	0•	3	5	4	10	8•	3	2	7	25	25
4	3	1	40	40	7	0	3	27	27	1	6	4	11	13•	1	3	7	28	28
5	3	1	32	31	1	1	3	14	13	1	0	5	56	56	2	3	7	26	25
6	3	1	7	0•	2	1	3	70	68	2	0	5	49	52	1	4	7	0	2•
1	4	1	5	6•	3	1	3	58	58	3	0	5	5	0•	0	0	8	41	41
2	4	1	46	47	4	1	3	5	5•	4	0	5	37	40	1	0	8	12	12
3	4	1	38	39	5	1	3	39	39	5	0	5	33	33	2	0	8	8	10•
4	4	1	0	2•	6	1	3	31	31	6	0	5	0	0•	3	0	8	35	35
5	4	1	26	24	7	1	3	0	1•	1	1	5	8	7•	1	1	8	34	33
1	5	1	46	45	1	2	3	68	67	2	1	5	48	48	2	1	8	13	10
2	5	1	2	3•	2	2	3	8	7	3	1	5	41	42	1	2	8	12	10

mentioned homogeneity range of the high-pressure phase. The larger size of these voids relative to the fully occupied ones indicates repulsion between the negatively charged oxygen ions. A similar observation has been made (*20*) in the structure of $Nb_8W_9O_{47}$. Further filling of the *2b* site with Re reduces the oxygen–oxygen repulsion and, thus, shortens the *a*-axis. (In a hypothetical structure where half of the *2b* positions were filled with rhenium, all oxygen–oxygen distances should be equal. The largest oxygen–oxygen distance, 3.00 Å, would then become equal to the shortest, 2.65 Å. These two distances are a function of the positional parameter *x* and the length of the *a*-axis only.)

A comparison with the two ambient-pressure phases ReO_2 (*7*, *21*) is also of interest. Their structures are of the MoO_2- and the α-PbO_2-type, respectively. In both of these the oxygen atoms are also approximately hexagonally close-packed with rhenium occupying certain of the octahedral sites. A comparison of the rhenium–oxygen distances is not possible, however, since the oxygen position in the two ReO_2 modifications are not known accurately enough.

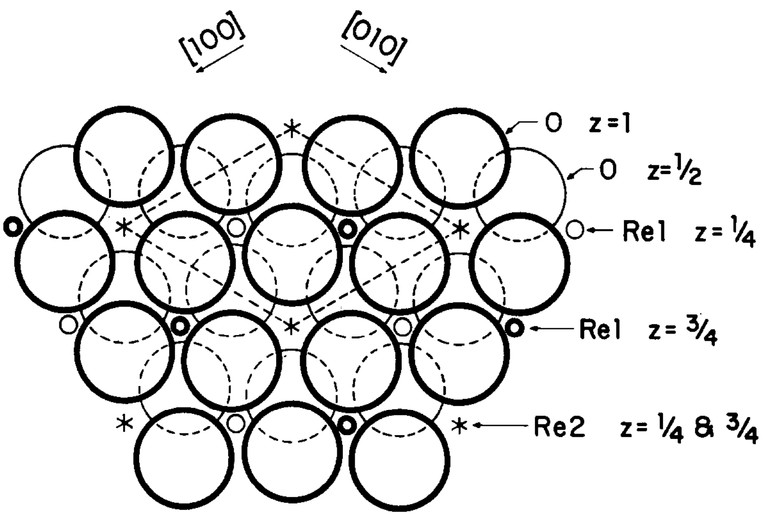

FIG. 1. The structure of the high pressure phase $Re_{1+x}O_3$ projected along the *c*-axis. The Re positions marked with an asterisk are only partially filled.

In Fig. 2 we compare $Re_{1+x}O_3$ to other structures possessing a hexagonal close-packed "host" structure where smaller atoms occupy octahedral interstices. All may be considered derived from the NiAs structure where all octahedral voids of the hexagonal close-packed As arrangement are filled with Ni atoms. Through ordering and vacancy formation, a great number of related structures can be derived. Since a uniform simple representation was aimed for, Fig. 2 contains only structures which fulfill the following requirements:

TABLE III

INTERATOMIC DISTANCES IN THE HEXAGONAL HIGH PRESSURE PHASE $Re_{1.16}O_3$. The distances are compared to the distances in the cubic normal pressure phase ReO_3. All distances within 3.0 Å are listed. Standard deviations are all less than 0.008 Å

$Re_{1.16}O_3$		ReO_3	
2 Re in 2*d*: 6 O	1.923 Å	Re: 6 O	1.874
3 Re (2*b*)	2.791		
0.32 Re in 2*b* : 6 O	2.073		
2 Re (2*b*)	2.267		
3 Re (2*d*)	2.791		
O in 6*g* : 2 Re (2*d*)	1.923	O: 2 Re	1.874
2 Re (2*b*)	2.073	8 O	2.650
2 O	2.646		
4 O	2.691		
4 O	2.856		
2 O	3.000		

(a) Only structures where the arrangement of the interstitial atoms is also of trigonal or hexagonal symmetry were considered. This excludes TiO_2-rutile (*21*), $CaCl_2$ (*21*), Co_2N (*22*), $LiSbO_3$ (*23, 24*), $ZnSb_2O_6$ (*25*), $NiWO_4$ (*21*), α-PbO_2 (*21*), $Nb_2(Fe,Mo)O_6$-columbite (*21*), MoO_2 (*21*), NbO_2 (*26*), FeS_2-markasite (*21*), and probably some more.

(b) The hexagonal close-packed atoms must be of the same kind—excluding Cr_2AlC (*27*)—and, therefore, only the relative arrangement of empty and occupied octahedral voids need be considered.

(c) The trigonal or hexagonal *a*-axis must not be larger than the *a*-axis in $Re_{1+x}O_3$—excluding UCl_6 (*28*)—and, therefore, a cut through the (110) face suffices to distinguish the remaining structural types.

Despite the simplicity of the $Re_{1+x}O_3$ structure, such a structure has not been reported for any other compound with hexagonally close-packed anions. This is true whether an ideal structure corresponding to ReO_3 (Re in *2d* only) or to Re_2O_3 (Re in *2d* and *2b*) is considered. It is, however, closely related to the antitypes Ni_3N and ϵ-Fe_2N and as can be seen in Fig. 2 may be considered as intermediate between these two structures. Complete filling of the *2b* position in the $Re_{1+x}O_3$ structure would lead to strings of face-shared octahedra along the *c*-axis. However, since this site is much less than half-filled, no face sharing need occur. Edge sharing of octahedra will, of course, take place between cations in the *2b* and *2d* positions.

The PdF_3 structure (the hexagonal close-packed branch of the VF_3-type structure) would be more

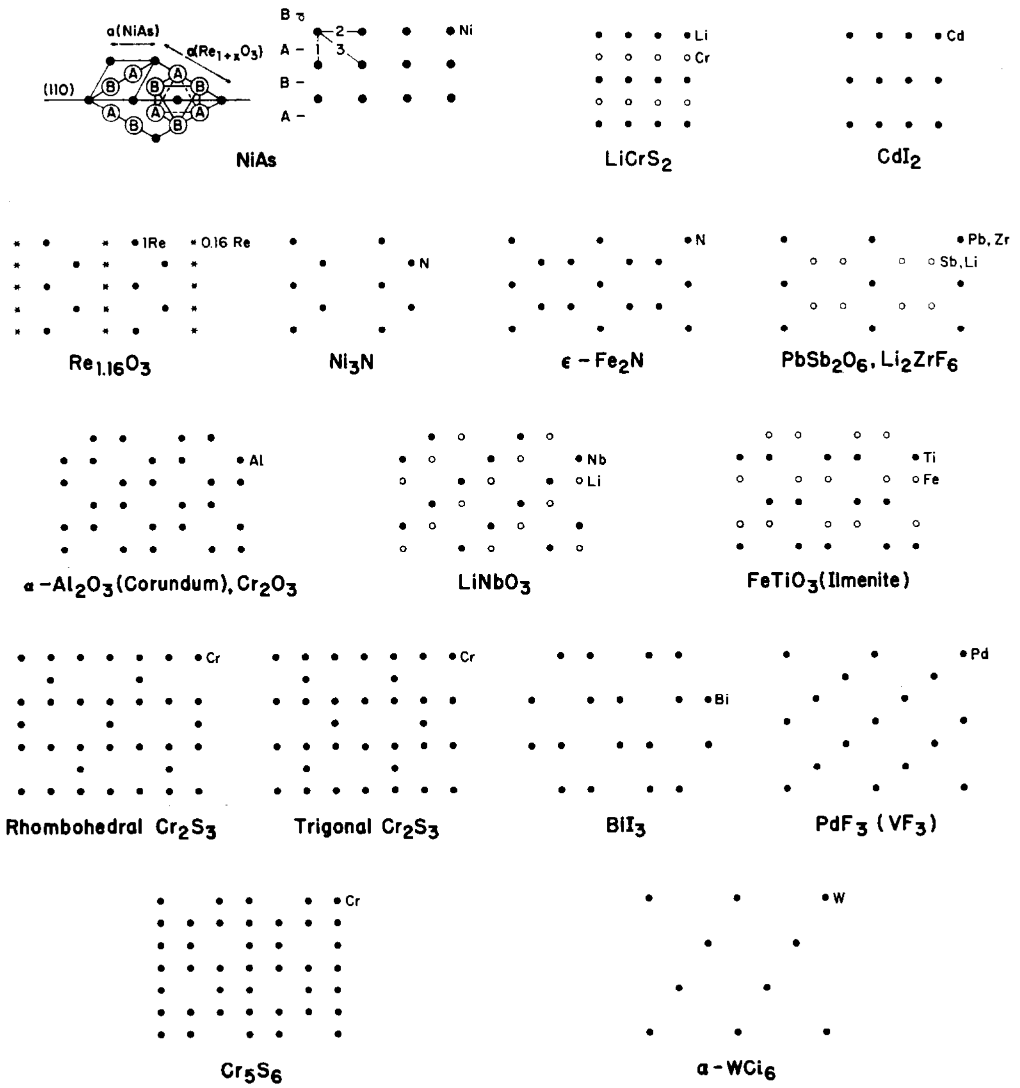

FIG. 2. The structure of the high-pressure phase $Re_{1+x}O_3$ as compared to other NiAs-related structures. All structures are represented through cuts through the (110) face of a unit cell corresponding to the $Re_{1+x}O_3$ cell. Only the atoms filling the octahedral voids of the hexagonal close-packed "host" structure are shown. The filled octahedra share faces (1), edges (2), or corners (3). References for the structures are given in parenthesis: NiAs (*21*), $LiCrS_2$ (*29*), CdI_2 (*21*), Ni_3N (*30*, *31*), ε-Fe_2N (*32*), $PbSb_2O_6$ (*33*), Li_2ZrF_6 (*34*), α-Al_2O_3-corundum, Cr_2O_3 (*21*), $LiNbO_3$ (*35*, *36*), $FeTiO_3$–ilmenite (*21*), rhombohedral and trigonal Cr_2S_3 (*37*), Cr_5S_6 (*37*), BiI_3 (*21*), PdF_3 (*38*), α-WCl_6 (*39*).

stable from an ionic point of view than the ideal hexagonal ReO_3 structure. However, additional metal ions in octahedral holes of the PdF_3 structure would immediately lead to face sharing of octahedra. Thus, the stability of the $Re_{1+x}O_3$ structure over the PdF_3 structure with interstitial metal ions is probably because edge sharing is favored over face sharing for the rhenium–oxygen octahedra.

The structure of $PbSb_2O_6$ (Fig. 2) is actually very closely related to that of $Re_{1.16}O_3$. If the *2b* site in $Re_{1.16}O_3$ were half-filled in an ordered manner along the *c*-axis, the $PbSb_2O_6$ structure could result considering all metals alike.

References

1. A. W. SLEIGHT, J. LONGO, AND R. WARD, *Inorg. Chem.* **1**, 245 (1962).
2. P. C. DONOHUE, J. M. LONGO, R. D. ROSENSTEIN, AND L. KATZ, *Inorg. Chem.* **4**, 1152 (1965).

3. R. Scholder and P. P. Pfeiffer, *Angew. Chem.* **75**, 376 (1963).
4. J. M. Longo and A. W. Sleight, *Inorg. Chem.* **7**, 108 (1968).
5. N. Morrow and L. Katz, *Acta Crystallogr. Sect. B* **24**, 1466 (1968).
6. A. W. Sleight, T. A. Bither, and P. E. Bierstedt, *Solid State Commun.* **7**, 299 (1969).
7. A. Magnéli, *Acta Chem. Scand.* **11**, 28 (1957).
8. A. W. Sleight and J. L. Gillson, *Solid State Commun.* **4**, 601 (1966).
9. H. Nechamkin and C. H. Hiskey, "Inorganic Synthesis," Vol. III, p. 186, McGraw-Hill, NY (1960).
10. T. A. Bither, J. L. Gillson, and H. S. Young, *Inorg. Chem.* **5**, 1559 (1966).
11. S. K. Smith and D. W. Krause, *Anal. Chem.* **40**, 2034 (1968).
12. K.-A. Wilhelmi, *Acta Chem. Scand.* **23**, 419 (1969).
13. A. Ferretti, D. B. Rogers, and J. B. Goodenough, *J. Phys. Chem. Solids* **26**, 2007 (1965).
14. D. B. Rogers, R. D. Shannon, A. W. Sleight, and J. L. Gillson, *Inorg. Chem.* **8**, 841 (1969).
15. A. Magnéli, *Acta Crystallogr.* **6**, 495 (1953).
16. "International Tables for X-ray Crystallography," Vol. II, Kynoch Press, Birmingham (1959).
17. L. W. Finger, unpublished computer program for the least-squares refinement of crystal structures (1969).
18. D. T. Cromer and J. B. Mann, *Acta Crystallogr. Sect. A* **24**, 321 (1968).
19. D. T. Cromer, *Acta Crystallogr.* **18**, 17 (1965).
20. A. W. Sleight, *Acta Chem. Scand.* **20**, 1102 (1966).
21. R. W. G. Wyckoff, "Crystal Structures," 2nd Edition, Wiley, NY, Vol. 1 (1963), Vol. 2 (1964), Vol. 3 (1965).
22. J. Clarke and K. H. Jack, *Chem. Ind. (London)* **46**, 1004 (1951).
23. M. Edstrand and N. Ingri, *Acta Chem. Scand.* **8**, 1021 (1954).
24. "Structure Reports," Volume 18, p. 444, Oosthoek, Utrecht (1961).
25. A. Byström, B. Hök, and B. Mason, *Ark. Kemi. Mineral Geol.* **15B**, No. 4 (1941).
26. B.-O. Marinder, *Acta Chem. Scand.* **15**, 707 (1961).
27. W. Jeitschko, H. Nowotny, and F. Benesovsky, *Monatsh. Chem.* **94**, 672 (1963).
28. W. H. Zachariasen, *Acta Crystallogr.* **1**, 285 (1948).
29. J. G. White and H. L. Pinch, *Inorg. Chem.* **9**, 2581 (1970).
30. R. Juza and W. Sachse, *Z. Anorg. Allg. Chem.* **251**, 201 (1943).
31. N. Terao, *J. Phys. Soc. Jap.* **17**, 238 (1962).
32. W. B. Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys," Pergamon Press, NY, Vol. 1 (1958) and Vol. 2 (1967).
33. A. Magnéli, *Ark. Kemi. Mineral. Geol.* **15B**, No. 3 (1941).
34. R. Hoppe and W. Dähne, *Naturwissenschaften* **47**, 397 (1960).
35. P. Bailey, thesis, 1952. Cited by H. D. Megaw, *Acta Crystallogr.* **7**, 187 (1954).
36. S. C. Abrahams, J. M. Reddy, and J. L. Bernstein, *J. Phys. Chem. Solids* **27**, 997 (1966).
37. F. Jellinek, *Acta Crystallogr.* **10**, 620 (1957).
38. M. A. Hepworth, K. H. Jack, R. D. Peacock, and G. J. Westland, *Acta Crystallogr.* **10**, 63 (1957).
39. J. A. A. Ketelaar and G. W. van Oosterhout, *Rec. Trav. Chim. Pays-Bas* **62**, 197 (1943).