creased from 2.06 to 3.50 mdynes/A, while the interaction constant between the free X–O bond and the bound ones was left unchanged at 2.06 mdynes/A. Next, the F_{rr} between the two bound X–O bonds was increased and simultaneously the free–bound F_{rr} was decreased in such a way as to keep the sum of the three force constants constant, a procedure exactly analogous to the polarization of the stretching force constants described above. Thirdly, with the F_{rr} back at their original value, the angle deformation force constant for the bound O–X–bound O angle, F_θ, was increased from 0.54 to 1.20 mdynes/A, while that for the other two O–X–O angles, F_α, remained set at 0.54 mdyne/A. Then F_θ was increased and F_α was decreased, so that the sum $F_\theta + 2F_\alpha$ remained constant, and, finally, a bond force constant polarization was chosen ($\Delta F_{XO} = 1.90$) and one set from each of the above calculations was repeated.

Comparison of the results obtained with frequencies reported in ref 2g, 7, and 17 shows, however, that none of these approximations is satisfactory. The first, increase of bound F_{rr}, gives values for ν_1, ν_3, and ν_8 that are all too low, even at the highest value of F_{rr} used, which is nearly 75% higher than the value found for the free XO_3 anion. In addition, ν_2 is shifted slightly (~15–40 cm^{-1}) in the wrong direction. The second approximation, polarization of the bond interaction force constants, gives too small a splitting of ν_1 and ν_7 and too large a splitting of ν_3 and ν_8. It also gives too low a value for ν_8 by as much as 100 cm^{-1}. The change in F_θ alone does not give a large enough splitting of ν_1–ν_7 for a reasonable ν_3–ν_8 splitting. Moreover, ν_7 is 100–160 cm^{-1} high. When the bond deformation force constants are polarized, we find that in order to get the ν_1–ν_7 splitting to the right order of magnitude, it is necessary to use force constants which give much too large a splitting of ν_3 and ν_8. Also ν_8 is too low.

When each of these changes, in turn, is imposed upon a force field where the bond force constants have been polarized by an amount $\Delta F_{XO} = 1.90$, the results are as follows: a change in the bound F_{rr}, which gives a reasonable ν_1–ν_7 splitting, shifts ν_2 by 50 cm^{-1} in the wrong direction and gives much too large (by 180 cm^{-1}) a splitting for ν_3 and ν_8. Simultaneous change in the bound–bound and free–bound F_{rr} gives only slightly better results: no shift in ν_2, correct splitting of ν_1 and ν_7, but too large a splitting of ν_3 and ν_8, with ν_8 100–200 cm^{-1} too low. Changing F_θ to get a reasonable value for the ν_1–ν_7 splitting makes both ν_1 and ν_7 60–100 cm^{-1} too high and also results in a ν_3–ν_8 splitting which is about 60 cm^{-1} too large. Changing F_θ and F_α gives, again, too large a ν_3–ν_8 splitting, with ν_8 100–150 cm^{-1} too low.

We feel that this rather detailed analysis of what we consider are all the reasonable possibilities for change in our approach is necessary to demonstrate the utility of the simple bond polarization approximation. Not only does it reproduce experimental frequencies more closely, but it does so using what seems to be the most realistic approximation. Changing other force constants, however, necessitates assumptions about electronic distributions in the molecules which are not justified in the light of our present knowledge. Moreover, the value of such a simple force field in spectrum diagnosis and assignment is lost as soon as it is complicated by such little-understood factors.

Acknowledgment.—The authors are glad for this opportunity to express their gratitude to Dr. J. A. D. Matthew for many helpful discussions.

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The Preparation and Properties of Some Ternary Nitrides of Strontium and Barium with Rhenium and Osmium

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Received February 18, 1966

Ternary nitrides of rhenium are formed by heating mixtures of strontium or barium nitride with metallic rhenium in pure nitrogen at atmospheric pressures. Under these conditions, osmium gives a ternary nitride only with barium. The isotypic compounds $Sr_9Re_3N_{10}$, $Ba_9Re_3N_{10}$, and $Ba_9Os_3N_{10}$ appear to be orthorhombic. They are all good conductors of electricity and are readily hydrolyzed. The magnetic properties suggest strong interaction between the transition metal ions. In the Ba–Re–N and Sr–Re–N systems, there exist thermally unstable compounds in which the rhenium has a higher oxidation state and the ratio of alkali metal to rhenium is higher than 3. The compound $Sr_{27}Re_5N_{28}$ has a cubic structure related to that of sodium chloride. The proposed structure is derived on the basis of ordered nitrogen vacancies. The rhenium atoms are distributed over the cation sites in such a way that no nitrogen is common to two rheniums. The magnetic susceptibility of this compound is temperature independent from 77 to 300°K. No intermediate phases were observed in the Ba–Os–N system.

Among the ternary oxides of the transition metals, there are notable differences between those formed with small cations such as lithium and magnesium and those obtained with the larger cations of groups I and II. The former often yield phases based on the sodium chloride, spinel, ilmenite, or olivine structures whereas the latter usually give phases with structures related to perovskite, pyrochlore, or garnet which offer sites of larger coordination numbers.

The ternary nitrides formed by lithium and various transition metals have been extensively studied by Juza and his co-workers,[1] who have found that many of the compounds have the antifluorite structure. The transition metals in these compounds all adopt their highest oxidation state giving rise to formulas such as Li_5TiN_3, Li_7NbN_4, and Li_9CrN_5. Superlattices were observed in most of the phases. All of the metal ions in these compounds occupy tetrahedral sites.

As a basis for the selection of appropriate cations, we assumed that compounds of the type AMN_3 would be likely products based on the close packing of AN_3 layers where A is a large cation analogous to the structures of many ternary oxides.[2] Since the available large cations all have charges of 3 or less, the choice of M cations would be restricted to elements of potentially high oxidation state. These are the transition metals of periods 5 and 6 in groups VI to VIII.

No compound of this type was identified. We found, however, that molybdenum, tungsten, rhenium, and osmium, none of which combines directly with nitrogen to give binary nitrides, yield ternary nitride phases when heated with barium or strontium nitrides in an atmosphere of nitrogen. The compounds formed by molybdenum and tungsten appear to have the sodium chloride structure but they were not obtained pure and their composition is not yet known. This paper deals with the ternary nitrides formed by barium and strontium with rhenium and by barium with osmium.

Experimental Section

(1) **Materials.**—Rhenium metal powder (99.99%) was washed with 6 *N* HCl to remove trace amounts of iron (14 ppm). The osmium metal powder (99.8%) contained no ferromagnetic impurities. Barium (99.5%) and strontium (98.99%) were massive. The binary nitrides of these elements were prepared by heating the metals in dry, oxygen-free nitrogen for several days. For barium, 600° was the best temperature; for strontium, 750°.

(2) **General Procedure.**—Since most of the reactants and all of the products were sensitive to moisture, all of the operations were carried out in an atmosphere of dry nitrogen. The reactants were intimately mixed in a Spex-500 mixer, pelleted, and heated in molybdenum-foil boats in a silica tube in nitrogen at atmospheric pressure. The reaction could be followed by observing the absorption of nitrogen which usually began at about 700°. The thermal instability of most of the products placed an upper limit on the temperatures. Most of the reactions had to be carried out in the temperature range 700–850°. Under these conditions the reactions occurred very slowly and tedious heating cycles were required to produce pure phases. Samples were periodically removed for examination by X-ray powder diffraction. The ground sample was dispersed in molten vaseline and, when the mass had solidified, was spread on a glass slide. This afforded sufficient protection from the atmosphere to obtain a diffractometer tracing. Some phases were observed which could not be isolated. Those which were obtained as a single phase were analyzed chemically: strontium and barium as sulfate, rhenium by precipitation as nitron perrhenate, and osmium by decomposition to metallic osmium. Nitrogen in most cases was determined by the Kjeldahl method but, occasionally, also by measuring the nitrogen absorbed in the preparation. X-Ray data were obtained with a GE XRD-5 diffractometer, using Cu Kα radiation and a proportional counter.

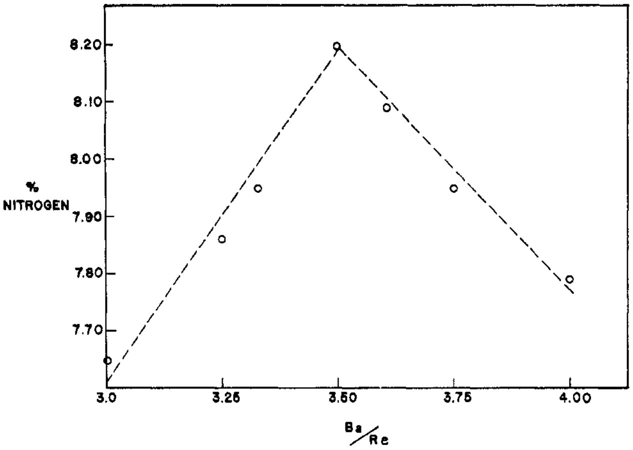

Figure 1.—Variation of nitrogen absorption as a function of Ba:Re by mixtures of Ba_3N_2 and Re.

The Ba–Re–N System.—X-Ray evidence indicated that the reaction between barium nitride and rhenium metal in nitrogen gives first an unstable ternary phase which changes on heating *in vacuo* to a thermally stable phase. The presence of barium nitride in the mixture is difficult to detect because of its poor diffraction pattern. Consequently, it was difficult to determine the proportions of barium and rhenium in the intermediate phase. As estimate of the Ba:Re ratio was obtained by measuring the amount of nitrogen absorbed by various mixtures of barium nitride and rhenium. The results shown in Figure 1 give this ratio as 3.5. By heating a mixture of this proportion in nitrogen, it was observed that absorption of the gas began at 700°. This temperature was maintained for 24 hr and again for 8 hr after regrinding the product. A final heating at 750° for 24 hr gave a deep red-brown product which contained 8.2% N by Kjeldahl. The X-ray powder diffraction pattern, although diffuse, clearly indicated a unique phase. It could be indexed on the basis of a hexagonal cell (a = 10.56 A, c = 11.83 A). By heating this phase under continuous evacuation at 850° for 24 hr, a black crystalline product was obtained. The use of an excess of barium nitride in the mixture gave a product of improved crystallinity. The excess barium nitride decomposes with sublimation of the barium upon heating *in vacuo* at 750–850°. It was found that the excess barium nitride could also be removed by dissolving it in liquid ammonia containing 0.2–0.4% NH_4NO_3. The black ternary nitride is insoluble in this solution. *Anal.* Calcd for $Ba_9Re_3N_{10}$: Ba, 63.89; Re, 28.87; N, 7.24. Found: Ba, 62.61; Re, 28.88; N, 7.24. The diffraction pattern for this compound is given in Table I. It can be indexed as shown on the basis of an orthorhombic cell: a = 10.94 A, b = 8.09 A, c = 30.40 A. The density measured pycnometrically in CCl_4 was 7.05 g/ml (calculated 7.15 for six molecular formulas per unit cell). A qualitative test indicated that the compound is a good conductor of electricity.

The Sr–Re–N System.—Strontium nitride differs from barium nitride in giving a sharp X-ray powder diffraction pattern. Its presence can readily be detected in a mixture. Mixtures of strontium nitride and rhenium metal powder when heated at 800–850° in dry nitrogen gave a mixture of two phases, one of which was never obtained pure. The other, a cubic phase, was obtained pure by the following procedure. An intimate mixture of 9 moles of strontium nitride and 5 moles of rhenium metal was heated in nitrogen at 460 and 750° for 24 hr at each temperature. The temperature was then raised to 810° and was maintained at that point until the absorption of nitrogen ceased. From 24 to 36 hr was usually required. The mixture was removed from the furnace, reground, and again heated at 810° for

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(1) R. Juza, H. H. Weber, and E. Meyer-Simon, *Z. Anorg. Allgem. Chem.*, **273**, 48 (1953); R. Juza, W. Gieren, and J. Haug, *ibid.*, **300**, 61 (1959); R. Juza and J. Haug, *ibid.*, **309**, 276 (1961).

(2) L. Katz and R. Ward, *Inorg. Chem.*, **3**, 205 (1964).

TABLE I

INDEXING OF $Ba_9Re_3N_{10}$ FROM X-RAY POWDER DATA

hkl	D_{obsd}	D_{calcd}	I_{obsd}	*hkl*	D_{obsd}	D_{calcd}	I_{obsd}
200	5.470	5.470	10.3	153	1.580	1.581	12.8
020		4.045	0	4,2,14	1.566	1.568	15.4
206	3.714	3.717	10.3	253	1.533	1.533	12.6
301	3.613	3.621	1.97	631	1.508	1.509	8.28
310	3.329	3.325	51.5	350	1.479	1.479	6.90
220	3.257	3.252	100.0	2,0,20	1.460	1.464	8.01
1,0,10	2.927	2.929	60.4	452	1.383	1.386	8.88
400	2.738	2.735	82.2	800	1.367	1.367	10.1
130	2.617	2.618	27.0	640	1.354	1.353	3.2
133	2.535	2.535	1.97	162	1.334	1.333	9.47
229	2.332	2.343	15.6	815	1.313	1.316	10.1
420	2.264	2.265	4.34	820	1.295	1.296	10.1
510	2.111	2.111	19.9	4,4,16	1.236	1.236	10.7
040	2.021	2.022	15.4	2,5,16	1.201	1.202	4.33
144	1.929	1.924	24.9	906	1.182	1.182	21.9
4,0,12	1.857	1.858	29.6	173	1.141	1.142	3.10
601	1.821	1.820	18.7	751	1.122	1.123	10.5
4,2,11	1.755	1.752	5.92	930	1.108	1.108	4.98
528	1.716	1.717	3.35	10,0,0	1.094	1.094	4.30
530	1.698	1.699	16.6	475	1.047	1.049	15.2
620	1.663	1.667	15.1	280	0.9947	0.9944	4.31
440	1.625	1.626	7.30	088	0.9762	0.9772	4.30

8 hr. Finally, the temperature was raised to 840–850° for 8 hr to complete the reaction. The deep reddish brown powder was found to be highly sensitive to moisture. A compressed pellet of the compound was found to be a nonconductor at room temperature.

Chemical analysis gave 62.5% Sr, 25.2% Re, and 10.5% N. The total analysis is 98.2%. It is assumed that the strontium analysis is low, since the starting Sr:Re ratio is about 5.5 whereas the analysis gives 5.25. By taking 64.3% Sr, one could deduce a rational formula $Sr_{27}Re^{VI}{}_5N_{28}$.

(3) **Structure Determination.**—The X-ray powder diffraction pattern could be indexed on the basis of a cubic unit cell, a = 5.25 A, which appeared to be of the sodium chloride type. The formula suggests a nitrogen-deficient structure. The density, calculated for $Sr_{3.375}Re_{0.625}N_{3.5}$ per unit cell, is 7.29 g/ml; found, 7.36 g/ml.

This compound appeared to be stoichiometric. No variation in lattice parameter was observed in several preparations including those with excess strontium nitride and those with the unidentified ternary phase.

Space group O_h^5 was used. In the trial structure, the strontium atoms were assumed to be replaced randomly by rhenium atoms. The scattering factor for the cation was then $(3.375f_{Sr} + 0.625f_{Re})/4$ and for the nitrogens $3.5f_N/4$. The observed intensities were determined by cutting out and weighing tracings of the peaks in the diffraction pattern obtained by use of a GE X-RD-5 diffractometer using Cu Kα radiation. Without the use of a temperature factor correction, it was shown that the calculated and observed intensities lay in the same order but that the difference increased progressively with increasing angle. A temperature factor was applied to I_{calcd} in the form

$$kI_{calcd}e^{-2B(\sin^2\theta)/\lambda^2} = I_{obsd} \text{ with } B = 4.5$$

The results are shown in Table II. This is taken as good evidence that the structure is essentially correct.

$Sr_9Re_3N_{10}$.—The thermal decomposition of the cubic phase *in vacuo* occurs at 740–760° to give a black crystalline product, the structure of which is analogous to the corresponding barium compound. The diffraction pattern is given in Table III, indexed on the basis of an orthorhombic cell: a = 10.38 A, b = 7.70 A, c = 28.62 A. *Anal.* Calcd for $Sr_9Re_3N_{10}$: Sr, 53.02; Re, 37.20; N, 9.42. Found: Sr, 52.18; Re, 37.20; N, 9.57. The compound is an electrical conductor at room temperature.

$Ba_9Os_3N_{10}$.—This compound, in contrast to the corresponding rhenium compound, is obtained without the formation of intermediate phases by heating mixtures of barium nitride and osmium powder at 700–750°. Mixtures with Ba:Os = 3 gave products containing no metallic osmium. Excess barium nitride could be removed by washing the product with liquid ammonia containing ammonium nitrate. The diffraction pattern corresponded closely to that of the rhenium compound. It is given in Table IV, indexed on the basis of an orthorhombic cell: a = 10.88 A, b = 8.08 A, c = 29.80 A. The compound is black and is a good conductor at room temperature. Like the rhenium compounds, it is very susceptible to hydrolysis, but it was noticed that some metallic osmium was liberated in the process. The nitrogen content as determined by the Kjeldahl method gave low results. Examination of the gaseous products of hydrolysis in the mass spectrograph revealed the presence of nitrogen. No consistent relationship between the amount of osmium metal formed and the ammonia determined by Kjeldahl analysis was found. The nitrogen was therefore determined by measuring volumetrically the quantity of nitrogen absorbed in the synthesis using the stoichiometry indicated by the equation $3Ba_3N_2 + 3Os + 2N_2 \rightarrow Ba_9Os_3N_{10}$. *Anal.* Calcd for $Ba_9Os_3N_{10}$: Ba, 63.50; Os, 29.31; N, 7.19. Found: Ba, 63.57; Os, 28.93; N, 6.96. Attempts to prepare strontium compounds of osmium were not successful. Preparations using mixtures of strontium and barium nitride with osmium metal gave heterogeneous products.

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR $Sr_{27}Re_5N_{28}$

	$\sin^2\theta$		*I*			$\sin^2\theta$		*I*	
hkl	Obsd	Calcd	Obsd	Calcd	*hkl*	Obsd	Calcd	Obsd	Calcd
111	0.0647	0.0647	100	100	400	0.3455	0.3450	10.4	13.9
200	0.0863	0.0863	86.5	91.2	331	0.4097	0.4097	16.6	19.7
200	0.1726	0.1725	63.5	64.2	420	0.4313	0.4313	20.2	23.8
311	0.2373	0.2372	50.5	47.3	422	0.5174	0.5176	26.4	19.4
222	0.2590	0.2580	18.7	19.3					

TABLE III

INDEXING OF $Sr_9Re_3N_{10}$ FROM X-RAY POWDER DATA

hkl	D_{obsd}	D_{calcd}	I_{obsd}	hkl	D_{obsd}	D_{calcd}	I_{obsd}
200	5.173	5.195	24.9	153	1.503	1.503	10.4
020	3.834	3.845	4.37	4,2,14	1.482	1.485	21.8
206	3.515	3.522	32.6	253	1.455	1.457	14.3
301	3.437	3.439	2.20	630	1.434	1.435	11.2
310	3.162	3.157	35.8	350	1.406	1.405	3.74
220	3.097	3.091	100	2,0,20	1.379	1.378	16.4
1,0,10	2.763	2.771	74.6	452	1.316	1.318	10.19
400	2.598	2.598	97.7	800	1.297	1.299	6.44
130	2.489	2.489	22.0	640	1.287	1.287	9.36
133	2.402	2.408	14.6	162	1.267	1.267	10.19
229	2.222	2.221	31.0	815	1.248	1.250	2.29
420	2.151	2.152	10.2	820	1.229	1.230	8.52
510	2.003	2.00	13.5	4,4,16	1.172	1.169	20.4
040	1.925	1.92	14.6	2,5,16	1.137	1.138	2.08
144	1.828	1.828	20.4	906	1.122	1.122	20.58
4,0,12	1.757	1.761	37.01	173	1.084	1.085	2.49
601	1.728	1.729	32.0	751	1.067	1.067	11.02
4,2,11	1.659	1.661	7.90	930	1.051	1.053	7.48
528	1.631	1.629	10.4	10,0,0	1.037	1.039	4.37
530	1.611	1.614	11.9	475	0.9961	0.9965	8.94
620	1.578	1.579	15.6	280	0.9457	0.9452	4.78
440	1.545	1.545	5.61	088	0.9282	0.9286	2.08

TABLE IV

INDEXING OF $Ba_9Os_3N_{10}$ FROM X-RAY POWDER DATA

hkl	D_{obsd}	D_{calcd}	I_{obsd}	hkl	D_{obsd}	D_{calcd}	I_{obsd}
200	5.438	5.440	7.95	153	1.580	1.578	14.2
020		4.040	0	4,2,14	1.547	1.548	15.1
206	3.695	3.668	7.10	253	1.530	1.530	14.5
301	3.607	3.600	1.14	631	1.505	1.502	18.8
310	3.312	3.309	46.8	350	1.475	1.476	7.10
220	3.245	3.243	100	2,0,20	1.439	1.437	10.5
1,0,10	2.875	2.873	57.1	452	1.382	1.383	12.8
400	2.720	2.720	73.9	800	1.358	1.360	3.12
130	2.619	2.614	22.7	640	1.348	1.349	7.10
133	2.531	2.528	5.96	162	1.331	1.331	12.5
229	2.333	2.317	19.3	815	1.311	1.308	11.9
420	2.254	2.256	5.68	820	1.287	1.289	8.23
510	2.100	2.100	18.8	4,4,16	1.222	1.223	12.5
040	2.021	2.020	14.8	2,5,16	1.193	1.191	3.12
144	1.929	1.919	30.9	906	1.174	1.175	12.1
4,0,12	1.838	1.834	28.1	173	1.140	1.140	2.83
601	1.807	1.810	26.1	751	1.121	1.119	10.5
4,2,11	1.731	1.734	11.08	930	1.104	1.103	5.00
528	1.710	1.704	5.00	10,0,0	1.088	1.088	4.00
530	1.692	1.692	19.6	475	1.044	1.046	12.3
620	1.653	1.654	14.5	280	0.9938	0.9930	4.21
440	1.621	1.622	3.12	088	0.9749	0.9748	3.90

The diffraction patterns indicated only a very slight solubility of strontium in the barium phase.

(4) **Magnetic Susceptibilities.**—The magnetic susceptibilities for all of the compounds which were obtained pure were measured from 77 to 300°K, about 30 readings being taken over the temperature range. Some of the temperature and magnetic susceptibility values per mole of transition metal corrected for diamagnetism are given in Table V.

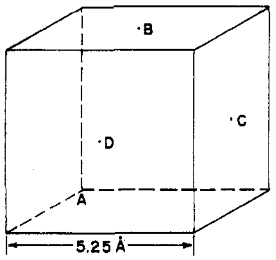
The plot of $1/\chi_M$ *vs.* T for $Sr_9Re_3N_{10}$ and for $Ba_9Re_3N_{10}$ was concave to the T axis. Corrections were made for a temperature-independent paramagnetism (377×10^{-6} cgs unit for the strontium compound, 210×10^{-6} cgs unit for the barium compound). With these corrections, linear plots of $1/\chi_M$ *vs.* T were obtained which gave for the strontium compound a Weiss constant $\theta = 32.7°$ and $\mu_{eff} = 0.52$ BM and for the barium compound $\theta = 12.6°$ and $\mu_{eff} = 0.45$ BM.

The $1/\chi_M$ *vs.* T plot for the osmium compound required no correction. It gave $\theta = 164.4°$ and $\mu_{eff} = 1.76$ BM.

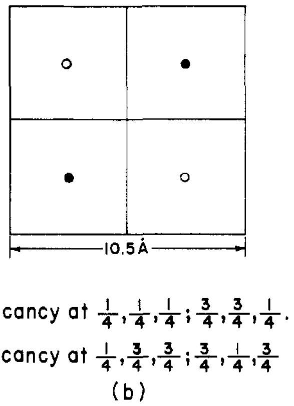
TABLE V

			$Sr_9Re_3N_{10}$			
T, °K	79	90	112	139	204	293
$10^6\chi_M$	817	794	749	688	666	625
			$Ba_9Re_3N_{10}$			
T, °K	79	90	106	157	216	294
$10^6\chi_M$	480	460	419	349	311	283
			$Ba_9Os_3N_{10}$			
T, °K	79	85	100	173	215	295
$10^6\chi_M$	1572	1528	1441	1119	998	826
			$Sr_{27}Re_5N_{28}$			
T, °K	79	102	154	207	254	293
$10^6\chi_M$	481	474	467	465	463	458

The data for $Sr_{27}Re_5N_{28}$ are uncorrected for a small ferromagnetic impurity. From the corrected data, the room temperature moment ($\mu_{eff} = \sqrt{\chi_M T}$) is 0.91 BM.



Rhenium substitution for Strontium at A and B, C or D.
(a)



(b)

Figure 2.—Model for the proposed structure of $Sr_{27}Re_5N_{28}$ based on random substitution of rhenium for strontium and ordered nitrogen vacancies.

Discussion

The experimental results show that the oxidation states in all of the compounds isolated are below the maximum for the transition metals, rhenium and osmium. This is a notable difference from the ternary nitrides obtained by Juza with lithium.

It is possible that some of the intermediate phases in the barium–rhenium and strontium–rhenium systems may contain heptavalent rhenium, but these are not stable compounds. The barium–rhenium nitride in which Ba:Re is approximately 3.5 is close to the composition which could be represented as $Ba_7Re^{VII}Re^{VI}N_9$, but a slight nitrogen deficiency could give all of the rhenium as Re(VI). The reddish brown color, very similar to that of $Sr_{27}Re_5N_{28}$, might be taken as support for the second possibility.

The low-temperature phase in the strontium–rhenium system identified as $Sr_{27}Re_5N_{28}$ has some peculiar properties which deserve attention. The X-ray diffraction data strongly suggest that the rhenium and strontium are randomly distributed over the cation sites of a sodium chloride type lattice. No indication of ordering lines was observed, yet the compound appears to be quite stoichiometric. An explanation for this phenomenon can be given on two assumptions: (1) that the rhenium ions, having such a high charge relative to the strontium ions, are not permitted to share a nitrogen and (2) that the nitrogen vacancies are ordered. The small cubic cell (a = 5.25 A) contains 4 cations and $3^1/_2$ nitride ions. If a rhenium atom occupies a corner position A (Figure 2a), the nearest rhenium atom to it could occupy a face center position B, C, or D. Nitride ions removed from two of the edges would then give a formula for the small cell $Sr_{3\,^3/_8}Re_{^5/_8}N_{3\,^1/_2}$. Eight of these units give the formula $Sr_{27}Re_5N_{28}$. The four nitrogen vacancies are arranged in the positions indicated in Figure 2b, alternate small cubes having vacancies. This is the same arrangement as the cation vacancies in the compound Mg_6MnO_8.[3] If we suppose a rhenium ion to lie at the center of the eight cubes indicated in Figure 2b, the other four would lie at the centers of the faces of the small cubes which are on the outside of the cell. To do this without allowing any of the rheniums to share nitrogens requires that the four rheniums be distributed randomly. The adjacent cells need not contain a rhenium at the center. Hence, the rhenium ions could be randomly distributed.

This structure suggests that one rhenium ion is in sixfold coordination with nitrogen and four are in fivefold coordination while seven strontium ions are in sixfold coordination and twenty in fivefold coordination. The charge balance is very favorable with this arrangement. A nitrogen vacancy in a nitride lattice creates a highly charged positive hole. It is perhaps reasonable to suppose that the electron of the neighboring Re(VI) ion would be drawn into this site. Perhaps the peculiar magnetic behavior of this compound is due to this phenomenon.

Little can yet be said about the compounds $Ba_9Re_3N_{10}$, $Sr_9Re_3N_{10}$, and $Ba_9Os_3N_{10}$. The determination of the structure must await single-crystal X-ray analysis. Attempts are being made to grow single crystals. The magnetic properties, however, suggest a strong interaction between the transition metal ions. It would seem reasonable to suggest that the rhenium(IV) atoms are in a triangular arrangement with shared nitrogens somewhat in the nature of the metal cluster in $Mg_2Mo_3O_8$.[4,5] Such a structure could derive readily from one containing close-packed nitride ions. The low magnetic moment of about 0.5 BM/rhenium(IV) ion could be due to a metal–metal bond which required eight electrons per cluster of three rheniums leaving one unpaired electron per cluster. The larger moment of 1.76 BM for the osmium compound lends support to this idea.

Acknowledgment.—Much of this work was supported by National Science Foundation Grant GP3461. We wish to thank Dr. Carl Moeller and Dr. Alan Callaghan for assistance in measuring the magnetic susceptibilities and Dr. Lewis Katz for advice in the interpretation of X-ray diffraction data. Thanks are also due to Dr. A. F. Wells[6] for helpful discussions of the structure.

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