perchlorates, though the opposite has been reported for solutions of nitrates in ethanol.[4]

The enthalpies of formation of aquo complexes for cobalt and nickel perchlorates from their butanol solutions are small and almost the same for the two salts. Significantly, there is observed a marked disparity in the values of the first two stepwise energies of binding and the values of the others. In aqueous solutions where complete dissociation may be assumed the enthalpies of formation of complexes with neutral ligands in most cases have been found to be consistent with eq 3 which is based upon the empirical relation

$$h_n = nh_1 \qquad (11)$$

implying that the binding energy is the same for each successive ligand added and does not depend upon the number and position of prior substituted ligands. The much larger values of the first (~3 kcal mole^{-1}) and second (~2 kcal mole^{-1}) stepwise enthalpy changes compared with the third (~0.6 kcal mole^{-1}) or fourth (~0.3 kcal mole^{-1}) support the contention that the metal species has a lower symmetry than the free solvated ion.

Over-all entropy of formation values are small, as would be expected for uncharged ligands, and when reduced to the mole fraction (unitary) basis by

$$\Delta S'_n = \Delta S_n + nR \ln (10^3/W) = \Delta S_n + 5.17n \qquad (12)$$

where W is the formula weight of butanol and ΔS_n is the entropy change on the molality scale, they are all positive. Table I shows that the entropy change in eq 10 does not become favorable until after the first two coordination positions have been occupied, but then the (positive) entropy change is about equally as important as the enthalpy change for further substitution of water for butanol.

Unfortunately, the experiments cannot resolve the question of inner-sphere *vs.* outer-sphere coordination of perchlorate. The relatively larger enthalpy changes for the first two substitution reactions by water are explicable on either basis. A rather large number of solid perchlorato complexes of copper and nickel have been found to contain monodentate and even bidentate perchlorate ligand. These include nickel perchlorate dihydrate[13] and numerous complexes having nitrogen donors where structural requirements of the ligand may be critical.[14] Perchloratobis(2,2′-bipyridyl)copper (II) ion may be formed in nitrobenzene solution also.[15]

There is no evidence that perchlorato complexes are formed in alcohol solutions, and we favor ion association for the butanol system. A model shows that substitution of water for butanol in the *trans* position permits a closer approach of the perchlorate anions to the metal with the result that the water dipoles aligned along the axis are in positions of lower potential energy than are molecules in equatorial positions. This could lead to stronger binding of the water ligand in such positions and a greater loss in entropy relative to the bulkier butanol molecule.

Acknowledgment.—The support of the U. S. Atomic Energy Commission under Contract AT(11-1)-1175 is gratefully acknowledged. The authors also wish to thank Dr. David G. Rands for permission to include some of his conductance data for $Ni(ClO_4)_2$ solutions in butanol–water solvent.

[13] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

[14] S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 1091 (1965).

[15] N. T. Barker, C. M. Harris, and E. D. McKenzie, *Proc. Chem. Soc.*, 335 (1961).

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On the Ternary System Samarium–Nitrogen–Oxygen and the Question of Lower Oxides of Samarium[1]

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The ternary compounds $SmN_{1-x}O_x$ ($0 < x \leq 0.5$) have been prepared; preparations where $x = 0.5$ have the same properties as substances previously thought to be SmO. The lattice parameter of $SmN_{1-x}O_x$, which has the NaCl structure, decreases continuously with increase in x. This suggests that as the nitrogen of SmN is replaced by oxygen, the 3+ valency of the samarium ion is retained although, formally, the oxygen–nitrogen exchange must result in the reduction of an equivalent amount of Sm^{3+} to Sm^{2+}. $SmN_{1-x}O_x$ undergoes hydrolysis on exposure to the atmosphere, and, on dissolving it in acid, hydrogen is evolved. The compound previously thought to be Sm_2O was found to be, in reality, SmH_2.

Introduction

This paper presents results of a study of phases previously thought to constitute part of the SmO_x–O_2 system in the range where x is between 0 and 1.5. No lower oxide of samarium could be prepared during the course of this investigation although substances fitting the description of those reported to be SmO and Sm_2O[2,3] have been prepared and found to be

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[1] This research was supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-1109. It was taken from a dissertation by T. L. F. submitted for the Ph.D. degree in 1966 and was presented at the Fifth Rare Earth Research Conference, Ames, Iowa, 1965.

[2] H. A. Eick, Ph.D. Thesis, Department of Chemistry, State University of Iowa, 1956.

[3] H. A. Eick, N. C. Baenziger, and L. Eyring, *J. Am. Chem. Soc.*, **78**, 5147 (1956).

samarium oxynitride and samarium dihydride, respectively.

Ellinger and Zachariasen[4] were the earliest to propose the existence of lower oxides when they reported what they thought to be SmO. This material had formed on the surface of samarium metal when it was annealed in an evacuated quartz tube at 625°. They found this and other preparations of the solid to have the NaCl structure with a lattice parameter which ranged from 5.015 to 5.050 ± 0.002 Å. Eick, *et al.*,[3] later suggested that the SmO reported by Ellinger and Zachariasen was actually a samarium oxide nitride and that the range of lattice parameters of this compound was due to differences in its oxygen and nitrogen content. A brightly colored compound prepared by Eick which had a smaller lattice parameter (4.9883 ± 0.0003 Å) than any reported by Ellinger and Zachariasen was believed to be pure SmO since no nitrogen was detected.

Samarium monoxide has also been reported as being prepared by carbon reduction of samarium sesquioxide according to Achard.[5] Lattice parameters were not published for this preparation, but it was stated that they were the same as those previously reported.[3,4] The report states that when a sesquioxide–carbon mixture was heated at high temperature under vacuum, a distillate containing the monoxide condensed on a cold finger.

La Blanchetais[6] found that if crude samarium metal was heated to 800–850° the samarium metal distilled out of its container leaving a skeleton of the original metal ingot. This skeleton was examined by X-ray diffraction and was thought to be principally SmO. Again, lattice parameters for the material were not published, but it was stated that they were the same as those previously reported.[3]

Eick, *et al.*,[3] also reported the existence of what they believed to be $\mathrm{SmO}_{0.4-0.6}$ (*i.e.*, $\mathrm{Sm_2O}$), an oxygen-deficient zinc blende structure with a lattice parameter which varied between 5.3698 ± 0.0006 and 5.3790 ± 0.0008 Å.

The Ternary System $\mathrm{SmN}_{1-x}\mathrm{O}_x$

Preparations.—Ternary phases were prepared by heating mixtures of samarium metal, samarium nitride, and samarium sesquioxide which had been weighed out to give the desired compositions according to

$$(x/3)\mathrm{Sm} + (2x/3)\mathrm{SmO}_{1.5} + (1 - x)\mathrm{SmN} = \mathrm{SmN}_{1-x}\mathrm{O}_x$$

The samarium metal for this reaction was in the form of turnings which had been taken from a block of the metal (obtained from F. H. Spedding and labeled 99.9% pure) under the protection of oil. Oxygen-uptake analysis showed these turnings to be 99.93 ± 0.04 wt % samarium metal.

The SmN (a = 5.046 ± 0.002 Å) was prepared by heating a mixture of $\mathrm{SmH_2}$ and $\mathrm{SmH_3}$ in nitrogen. The hydride mixture had been prepared by heating samarium metal turnings to 275° in $^1/_{15}$ atm of dry hydrogen.[7] The hydride was converted to the nitride by heating at 500° in an atmosphere of nitrogen which had been purified by first passing through a trap cooled by a Dry Ice–alcohol slurry (for removal of residual water) and then over titanium metal in lump form heated to 800° (for the removal of any oxygen impurity). The weight of nitrogen taken up, observed as a weight change on a quartz spring balance, corresponded to a final product of composition $\mathrm{SmN}_{0.93}$ After preparation, the material was removed from the system and quickly placed in a drybox to prevent hydrolysis. The drybox was filled with argon which was predried by passing through a molecular sieve and kept dry with phosphorus pentoxide. All subsequent weighings of the $\mathrm{SmN}_{0.93}$ were done in weighing bottles. As a consequence of the nonstoichiometry of the samarium nitride preparation, the oxynitride samples contained only 93% of the nitrogen indicated by the above equation.

The $\mathrm{Sm_2O_3}$, labeled 99.9% pure from Research Chemicals, was heated at 800° for 24 hr to remove water and $\mathrm{CO_2}$ prior to its use.

After appropriate amounts of the different reaction materials had been weighed, they were vigorously shaken together in a glass weighing bottle. To ensure intimate contact of the particles of these mixtures they were pressed into pellets. The pellets were then sealed into degassed tantalum containers for heat treatment. The tantalum crucibles had to be hermetically sealed so that the samarium metal in the vapor state could be contained.

The samples were heated in a molybdenum-wound furnace. An alumina tube held loosely inside the furnace core was fitted with water-cooled Pyrex ends so that attachments could be made. The attachments consisted of inlets and outlets for argon gas, an optical window, a windlass, and a connection to a vacuum pump for evacuation of the inner alumina tube which facilitated flushing the system. The alumina tube was filled with argon which provided an inert atmosphere for the tantalum container which was lowered into and lifted out of the hot zone by the windlass.

The temperature of the container was determined by sighting through the optical window with a Leeds and Northrup optical pyrometer. The temperature correction for the prism and optical window applied to all experiments was determined by sighting the pyrometer on a Pt—Pt-10% Rh thermocouple which was in the hot zone.

After the heat treatment, the tantalum containers were opened in the drybox. The pelleted samples, which had become sintered during the heat treatment, were subjected to phase analysis by X-ray powder diffraction and micrographic examination.

Analyses.—All of the X-ray analyses were made with a Norelco 114.6-mm Debye–Scherrer powder camera using filtered copper radiation (λ_{α_1} 1.54051 × 10^{-8} cm) except that, when long exposures were needed to see weak reflections, the fluorescent scattering of

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[4] F. H. Ellinger and W. H. Zachariasen, *J. Am. Chem. Soc.*, **75**, 5650 (1953).

[5] J. C. Achard, *Compt. Rend.*, **245**, 1064 (1957).

[6] C. H. La Blanchetais, *ibid.*, **254**, 2785 (1962).

[7] D. E. LaValle, *J. Inorg. Nucl. Chem.*, **24**, 930 (1962).

copper radiation necessitated the use of iron radiation. The lattice parameters were determined by performing a least-squares analysis using a Nelson–Riley[8] extrapolation.

Detailed phase analysis was carried out by the use of a Leitz metallographic microscope equipped with an automatic 35-mm camera for taking photomicrographs. Reflected light was used in combination with oil immersion objectives in resolving power from 300× up to 1200×.

The microscopic analysis revealed that besides the $SmN_{1-x}O_x$ phase, samarium, Sm_2O_3, and an unidentified phase were present in many of the samples. These phases were identified partly by correlating their observed characterisitics to known chemical and physical properties. The $SmN_{1-x}O_x$ phase could be easily identified by its color, and it was the only phase among the group that underwent air etching or appeared to be isotropic and, therefore, cubic. The B-form Sm_2O_3, a dark gray phase with low reflectivity, appeared to be anisotropic in certain regions and was the hardest of the phases present. The relative hardness of the phases was determined by noting the amount of abrasion each had undergone in polishing the sample. Samarium metal appeared to be anisotropic and was light gray with a high reflectivity. It appeared in most cases as a matrix for the other phases present, thus indicating that it was molten at high temperatures, and it was the only phase that had been molten. The fourth and unidentified phase which appeared in many of the samples was light blue and constituted only a small fraction of 1% of any preparation in which it was present.

Another aid in identifying the phases was to make a comparison between the amounts of the phases observed through the microscope and the relative line intensities from each phase on the X-ray powder patterns. This was used in identifying the $SmN_{1-x}O_x$ and B-form Sm_2O_3 phases.

Samples in which the nominal mixtures had nonmetal to metal atom ratios of 0.95 rather than unity were prepared to attain a greater homogeneity in the final product than had been achieved in samples having nonmetal to metal atom ratios of unity. Also, the $SmN_{0.93}$ and Sm_2O_3 powders were thoroughly mixed by grinding them together until a uniform gray color resulted. The samarium metal turnings were then added to the mixture; the mixture was pressed into a $^3/_8$-in. diameter pellet and then heat treated as described above at 1350° for 24 hr.

Subsequently, these samples were inductively heated under dynamic vacuum to distil out the excess samarium metal. Before heating the sample which was contained in a quartz furnace tube by a previously degassed tantalum crucible, the walls of the furnace tube were degassed by gently heating them with a flame while pumping. During the distillation, metal condensed on the cold walls as the sample temperature reached 900°. The temperature was raised to 1000° and maintained for 30 min to assure complete removal of the samarium metal, although most of it had distilled out at 900°. After cooling, the depleted pellet was removed from the vacuum system and placed in the drybox. A microscopic analysis confirmed that nearly all of the excess samarium metal had vaporized out of the sample. Since the sample appeared to be relatively pure by microscopic analysis, an elemental analysis was performed.

The method of nitrogen analysis used in this work was basically a modification by Kern and Brauer[9] of the Dumas method. The major alteration of Kern and Brauer's modification was in the combustion of the sample. To effect complete combustion, the sample was heated inductively to 1185°. Best results were achieved when the temperature was increased to this value over a period of 1 hr.

Nitrogen analysis was also performed by the Winkler modification of the Kjeldahl method. Ammonia from the distillation step of the procedure was collected in a 2% boric acid solution and was titrated with a standard hydrochloric acid using an indicator made up of five volumes bromocresol green to one volume methyl red.[10,11] The average amount of nitrogen recovered from an ammonium chloride sample was 99.3 ± 0.8% of the theoretical amount expected.

The samarium content of the samples was found by oxidizing the samples contained in platinum, in air at 1100° to a constant weight. These oxidized samples were taken to be pure Sm_2O_3, in agreement with observations of their X-ray powder diffraction patterns. The oxygen content was determined by difference.

Results and Discussion

The $SmN_{1-x}O_x$ preparations having nominal compositions shown in Table I had become sintered during the heat treatment and were a variety of colors which gradually changed from one preparation to another as the composition varied over the range. Samples having oxygen fractions 0.75 and 0.67 showed regions of gray material in the sintered pellet along with the gold substance, but the amount of gray decreased with x, the atom fraction of oxygen.

X-Ray powder diffraction analysis confirmed that in mixtures where $x \geq 0.67$, the system consisted of two phases. The first was face-centered cubic and the second was the β-form Sm_2O_3. The lattice parameter of the phase with the NaCl structure was the smallest observed in the series of preparations and was independent of x for $x > 0.5$. For $x < 0.50$ there was an increase—apparently continuous—in the lattice parameter of the face-centered-cubic phase with decrease in x up to $x = 0.20$, the lower limit of the present experiments. Possibly, as suggested by Eick, *et al.*,[3] this trend extends

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(8) L. V. Azaroff and M. J. Buerger, "The Powder Method in X-ray Crystallography," McGraw-Hill Book Co., Inc., New York, N. Y., 1958, p 238.

(9) W. Kern and G. Brauer, *Talanta*, **11**, 1177 (1964).

(10) G. W. C. Milner, I. G. Jones, and G. Phillips, "Determination of Nitrogen in Plutonium Nitride," United Kingdom Atomic Energy Authority, Research Group, Atomic Energy Research Establishment, Report AERE-R 5002, 1965.

(11) W. J. Blaedel and V. M. Meloche, "Elementary Quantitative Analysis: Theory and Practice," Row, Peterson and Co., Evanston, Ill., 1957.

TABLE I

PREPARATION AND CHARACTERISTICS OF $SmN_{0.93(1-x)}O_x$

Nominal x	Temp of reaction, °C	Reaction time, hr	Lattice parameter, Å	Color
0.75	1280	10	4.978[a]	Gold (metallic luster) + gray regions
0.67	1280	10	4.9783 ± 6[b]	Gold (metallic luster) + gray regions
0.60	1285	8	4.9785 ± 4	Yellow
0.50	1285	8	4.9807 ± 3	Orange
0.40	1285	8	4.986 ± 2	Red
0.33	1285	8	5.010 ± 3	Purple
0.25	1340	18	5.006 ± 1	Blue
0.20	1340	18	5.012 ± 2	Greenish blue
0.00			5.046 ± 2	

[a] This lattice parameter was estimated by comparing the X-ray pattern to one that had previously been measured. [b] Errors are in the last figure recorded in the lattice parameter.

even to the composition where $x = 0$. The lattice parameters and the colors of the preparations are recorded in Table I.

The X-ray powder diffraction patterns of the two $SmN_{0.475}O_{0.475}$ preparations (which will be referred to hereafter as A and B) showed them to be the NaCl-type phase with the lattice parameters shown in Table II. There was at least one very weak line appearing in each of the patterns which could not be indexed on the face-centered-cubic cell. The distillation procedure, which served to rid the sample of excess samarium, was carried out on two different portions of preparation A. A comparison of the X-ray powder diffraction patterns before and after distillation showed that in one case there was no shift in the position of the lines but in the second case there was a very small shift of the lines toward a higher angle. Distillation of preparation B removed the material responsible for one of the extra unidentified lines in the X-ray powder pattern, but there was no shift in the positions of the lines due to the NaCl-type phase.

TABLE II

LATTICE PARAMETERS OF HOMOGENEOUS $SmN_{0.95-x}O_x$ PREPARATIONS

	Lattice parameter, Å	
Nominal compn	Initial prepn	Excess Sm distilled off
$SmN_{0.38}O_{0.57}$	4.9784 ± 0.0002	
$SmN_{0.475}O_{0.475}$ (A)	4.9790 ± 0.0004	4.9783 ± 0.0006 4.9779 ± 0.0003
$SmN_{0.475}O_{0.475}$ (B)	4.9787 ± 0.0005	4.9782 ± 0.0003
$SmN_{0.57}O_{0.38}$	4.9879 ± 0.0002	

The results of the samarium and nitrogen analyses of the homogeneous $SmN_{0.475}O_{0.475}$ preparations A and B are as follows. Specimen A was 91.0 ± 0.9 wt % samarium on three samples and 3.92 wt % nitrogen on one sample run by the Dumas method. Specimen B was 91.16 ± 0.04 wt % samarium on three samples and showed 3.86 ± 0.01 wt % nitrogen by three samples run by the Kjeldahl method and 3.9 ± 0.3 wt % nitrogen on three Dumas samples. The limits of error are expressed at the 95% confidence level. The reason the accuracy of the samarium value is so much better for preparation B than for A is principally the size of samples taken for analysis.

The formula calculated for preparation A was $SmN_{0.46}O_{0.52}$ and that for sample B was $SmN_{0.454}O_{0.513}$. The fact that the sum of the number of nonmetal atoms was less than that of metal atoms is readily apparent. If a general chemical formula is to be written for a series of compositions from the oxygen-rich compound to the oxygen-poor compound, it must account for the slight deficiency in the nitrogen content indicated in the two chemical formulas above and in the pure nitride $SmN_{0.93}$. By using the general formula $SmN_{0.93(1-x)}O_x$, the value of x comes very close to the experimental value for the more precisely analyzed preparation B.

Systematic errors could have resulted for either the Dumas method or the Kjeldahl method from hydrolysis of the compound while exposed to moisture of the air, and, in the Kjeldahl analysis, error could have been due to nitrogen loss during sample dissolution in acid. A test was carried out to determine nitrogen loss due to air hydrolysis of the specimen during handling. A portion of the sample was placed in a dry 10-ml beaker and quickly covered with a small watch glass which had a wet piece of litmus adhering to its convex underside. It was about 5 min from the time of exposure of the sample to air until the litmus started to change color, thus indicating the presence of ammonia. The amount of ammonia evolved was very small since it could not be detected by its odor. The length of time samples were exposed to air was about the same as that required to begin to change the color of the litmus in the above experiment but there was no wet material in the vicinity.

In hydrochloric acid dissolution of $SmN_{0.45}O_{0.51}$, a gas was evolved from the sample. This gas, isolated and analyzed mass spectrometrically, was found to be only hydrogen after subtraction of a 1% nitrogen blank. From this result, it was concluded that the Kjeldahl method for nitrogen analysis was reliable. The major source of error in determining the nitrogen content of the samarium oxide nitride samples, loss of nitrogen due to air hydrolysis, was even less for the Kjeldahl method than for the Dumas method because the former required less handling.

The absence of nitrogen in the hydrogen evolved during acid dissolution of $SmN_{0.45}O_{0.51}$ indicates that the nitrogen is ionically bound in the solid with a formal charge of three, two, or something between as is suggested for the lanthanide nitrides by Didchenko and Gortsema.[12]

During the most vigorous evolution of hydrogen from $Sm_{0.45}N_{0.51}$ a dark red color appeared in the solution; it lasted only a fraction of 1 sec in strong acid, but in weak acid (0.53 N), which was heated to increase the hydrogen evolution rate to an appreciable level, the red color was visible for several seconds. This coloration of the solution is attributed to the

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(12) R. Didchenko and F. P. Gortsema, *J. Phys. Chem. Solids*, **24**, 863 (1963).

divalent samarium ion which is reportedly dark red. The Sm^{2+} ion apparently forms at the solid–solution interface, since there is good evidence from several considerations to be discussed below that in the solid phase samarium is in the trivalent oxidation state with an electron in the conduction band. The evolution of hydrogen and the fading of the color indicates that the Sm^{2+} ion is rapidly oxidized to Sm^{3+} in solution. These two reactions can be formulated as $Sm(c)^{3+} + e(c) = Sm(aq)^{2+}$ and $Sm(aq)^{2+} + H(aq)^{+} = Sm(aq)^{3+} + {}^{1}/{}_{2}H_2(g)$.

From the above observations and by using an idealized stoichiometry for the solid, one can write the over-all equation for the acid hydrolysis of $SmN_{0.5}O_{0.5}$: $2SmN_{0.5}O_{0.5} + 7H^{+} = 2Sm^{3+} + NH_4^{+} + H_2O + {}^{1}/{}_{2}H_2$.

Reported Sm_2O Shown to Be SmH_2

Sm_2O has been described by Eick, *et al.*,[3] as having the zinc blende structure with half the anion sites vacant. Pebler and Wallace[13] have reported a fluorite-type SmH_x where x ranged from 1.95 to 2.59. (As is commonly done, this phase is referred to in this work as SmH_2.) The cation sublattice is the same in these two structures; therefore, any difference between the powder patterns of the two compounds would be derived from the anion sublattice.

From relative intensity measurements of the X-ray powder diffraction lines due to the (331) and (420) planes, Eick, *et al.*,[3] concluded that the anion sublattice was at least partially occupied. They concluded further that the compound was an oxide because they could rule out the possibilities of its being either a nitride or a carbide, but they overlooked the possibility of its being a hydride. In calculating the amount of oxygen present in the sublattice from the intensity data, they found that the oxygen to samarium atom ratio was 0.3.

The relative intensities of the above two lines were calculated by using Eick's[2] data and published structure factors for the hydride ion.[14,15] This calculation showed that the anion sublattice could consist of hydride ions and still fit Eick's relative intensity data as well as the amount of oxide ion that he had proposed to be present.

Eick, *et al.*,[3] had also attempted to determine the amount of oxygen present in the compound by igniting to Sm_2O_3 and determining the value of x in $Sm_2O_x + [(3 - x)/2]O_2 = Sm_2O_3$ from the weight of the oxygen uptake. The weight-uptake observations, however, would have also been consistent with the reaction $2SmH_2 + {}^{5}/{}_{2}O_2 = Sm_2O_3 + 2H_2O$ since the observed weight increase of this reaction differs from the above by no more than 4%, a difference less than the variation in analysis between samples. Eick, *et al.*,[3] considered the variation between samples to be due to actual composition variation which would, of course, be true even for the hydride.

For these reasons there is a good basis to suspect the report of Sm_2O. In an attempt to settle this question, a preparation of the material reported as Sm_2O was carried out in a manner simulating the conditions of Eick, *et al.*,[3] as closely as possible. This preparation was subsequently analyzed for its hydrogen and samarium content.

Experimental Section

The glass system used to prepare the samples was constructed so that a recirculated argon stream could be passed over the reactants as they were being heated. The reactants were contained by a tantalum crucible set in a cylindrical tantalum shield. The latter served as the suscepting secondary coil for induction heating.

A standard combustion system was used for hydrogen analysis. Hydrocarbons or other hydrogen sources present in the tank oxygen were removed by precombusting them over platinum foil at 850°. The oxygen was passed through anhydrous magnesium perchlorate to remove any resultant moisture.

Any H_2O produced in the combustion of hydrogen in the unknown sample was collected in microabsorption tubes weighed on a Mettler microbalance.

Samarium dihydride, prepared by decomposing the trihydride, was used as a standard in determining the accuracy and precision of the hydrogen analysis technique. Samples were heated to about 500° to effect combustion. Samarium content was determined from the weight of the Sm_2O_3 (shown by X-ray analysis) which resulted from the combustion. X-Ray powder diffraction was used for phase analysis. A Debye–Scherrer powder camera, recording diffracted copper $K\alpha$ radiation, was employed.

Samarium turnings, cleaned as described in the $SmN_{1-x}O_x$ preparations, and samarium sesquioxide (99.9% pure) were used in preparing the samples. The rather hygroscopic Sm_2O_3 was not dried for use. An equimolar mixture of the two reactants was placed in a crucible in the system. After evacuation, the system was filled with argon to 0.6 atm. The system was then isolated and the recirculating pump started.

On heating the sample, a black vapor flowed off into the argon stream at 1115°. This vapor settled out of the argon and collected on the walls of the reaction tube. The furnace was turned off and the system was allowed to cool after enough material for analysis had collected. The isolation chamber was removed from the system and placed in a drybox. Here the sample was removed from the walls and divided into three portions for analysis.

Results

The most prominent lines in the X-ray diffraction pattern from the black sublimate were the same in intensity and position as those reported in the preparation of Eick, *et al.*[3] Second in intensity were the lines of the C-form Sm_2O_3 which had less than half the intensity of those of the first phase. The strongest line of SmH_3 appeared very weakly.

The data shown in Table III must be interpreted with the relative amounts of the different phases seen by X-ray powder patterns in mind. The hydrogen to samarium ratios were large enough to indicate that a considerable amount of SmH_2 is present. The variation of ratios indicates the presence of different quantities of the several phases observed in the powder patterns. An inadvertent segregation of some of these phases in the sampling procedure resulted in the markedly different ratios for sample A.

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[13] A. Pebler and W. E. Wallace, *J. Phys. Chem.*, **66**, 148 (1962).

[14] C. H. MacGillavry and G. D. Rieck, Ed., "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

[15] B. D. Cullity, "Elements of X-ray Diffraction," Addison-Wesley Publishing Co., Inc., Reading, Mass. 1956.

TABLE III

HYDROGEN TO SAMARIUM MOLE RATIOS OF UNKNOWN PREPARATIONS

Sample	Wt of H_2O collected, mg	Wt of Sm_2O_3, mg	H/Sm mole ratio
A	0.089	1.798	0.96
A	0.390	3.042	2.48
B	0.896	10.165	1.78
B	0.832	9.047	1.71

Because of the method of preparation, samarium metal was surely present in addition to the phases observed by X-ray analysis. It did not appear in the powder pattern because it would probably condense from the vapor in an amorphous form. The small hydrogen to samarium ratio reported for the first of the two samples A indicated that samarium metal was present.

These results almost certainly prove that the phase reported by Eick, *et al.*,[3] as Sm_2O is, in fact, SmH_2. The source of hydrogen needed to produce the hydride was undoubtedly absorbed water on the undried Sm_2O_3, on the walls of the apparatus, and that present in the argon. The formation of a dihydride by a reaction between a rare earth metal and water at elevated temperatures has also been observed in work with cerium.[16]

A proposed mechanism for the formation of SmH_2 from water and samarium follows. Hot samarium metal reacts with water to form Sm_2O_3 with the liberation of hydrogen, which in turn reacts with the samarium vapor before it condenses. The samarium would have to be at a tempeature below 700° to react with hydrogen since SmH_2 is known to decompose at about 700°.

General Discussion

No evidence has been found in this work for the existence of SmO. Rather the phase previously reported as such has been shown to be approximately $SmN_{0.5}O_{0.5}$ near the lower nitrogen composition limit of this phase. The exchange of oxygen for nitrogen in $SmN_{1-x}O_x$ proceeds until the value of x reaches approximately 0.5 where the system separates into two phases, $SmN_{0.5}O_{0.5}$ and Sm_2O_3 (see Table I).

Eick, *et al.*,[3] first suggested that oxygen might be exchanged for nitrogen in the SmN lattice to explain the range of lattice parameters Ellinger and Zachariasen thought were due to SmO. Such an exchange has been found for both europium[12] and gadolinium[17] nitrides with pronounced effects on their magnetic properties.

The lattice parameter of $SmN_{1-x}O_x$ decreases with increase in oxygen because the oxide ion is much smaller (ionic radius = 1.40 Å) than the nitride ion of samarium nitride (ionic radius = 1.56 Å). This is also observed in the $GdN_{1-x}O_x$ system. For the $SmN_{1-x}O_x$ lattice parameter to decrease with increasing oxygen content, the samarium ion must not increase appreciably in size; *i.e.*, the trivalent samarium ion (ionic radius = 0.964 Å[18]) must not change to the divalent state (ionic radius ≅ 1.17 Å). Formally, of course, for each oxide ion that is put into the lattice, a samarium trivalent ion must be reduced to the divalent state. Since, however, there is a decrease in the lattice parameter, most of the cations apparently retain the ionic radius of the trivalent state as exists in the pure nitride.

Samarium nitride and all of the other rare earth nitrides have been shown magnetically to have trivalent cations, and yet, with the exception of europium and ytterbium, they all display low resistivities with metallic temperature dependencies. The authors of these results, Didchenko and Gortsema[12] and McClure,[19] concluded that the rare earth ions of these nitrides are completely ionized and that the nitride ion has a valence between 2 and 3 but closer to 2. This was interpreted to mean that, for all of the nitrides except cerium, one valence electron for each rare earth ion is distributed among the p orbitals of the nitrogen and the conduction bands which are made up of the 5d and 6s orbitals of the metal. These delocalized electrons account for the metallic electrical properties of the nitrides. The postulate that the nitride ions have a formal charge close to 2 also accounts for the ionic radius of these ions which ranges from 1.53 to 1.58 Å—much smaller than Pauling's value ($r_{N^{3-}}$ = 1.71 Å). This condition would also favor substitution of oxygen for nitrogen in the structure.

Further evidence supporting the argument that most of the samarium ions remain trivalent as oxygen is exchanged for nitrogen in SmN is found in compounds where the rare earth ions are found to be divalent magnetically as well as being divalent formally. Compounds of this nature are found in the rare earth monosulfides, monoselenides, and monotellurides.

The NaCl-type compounds of all of these rare earth chalcogenides except those of samarium, europium, and ytterbium are similar to the nitrides in that they have been found to be metallic conductors, and the rare earth ions are found by means of magnetic susceptibility measurements to be trivalent.[12,19,20] The monosulfides, monoselenides, and monotellurides, of samarium, europium, and ytterbium, however, are found from magnetic susceptibility measurements to be divalent compounds, and they are either semiconductors or saltlike insulators. The lattice parameters of these compounds also separate them into two groups (see Figure 1). The lattice parameters for the samarium, europium, and ytterbium compounds are much larger than those of the other rare earths, the reason being that the cations of samarium, europium, and ytterbium are divalent according to magnetic measurements as well as formally.

Finally the presence of trivalent cations in Sm-

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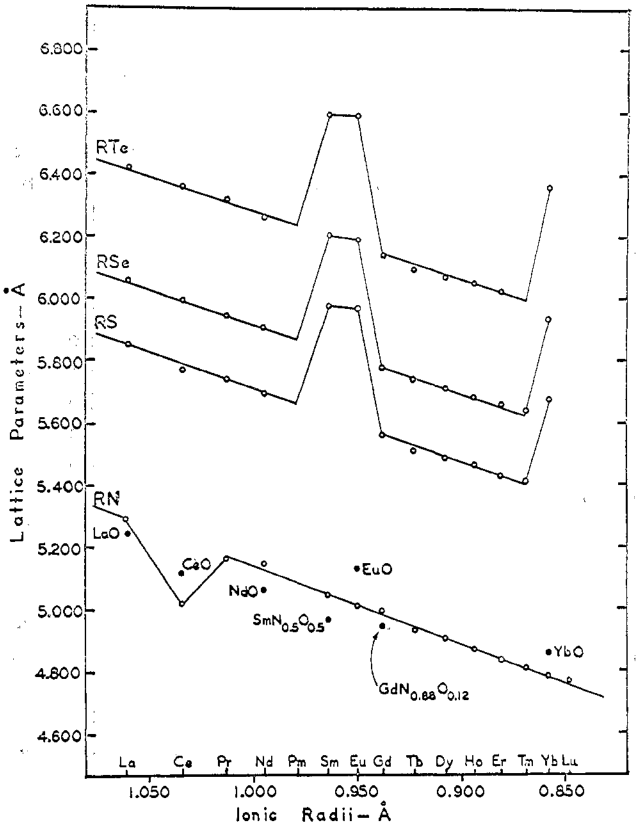

Figure 1.—Some rare earth compounds with the NaCl structure.

$N_{1-x}O_x$ is argued by comparing the lattice parameters of EuO (5.1439 Å) and EuN (5.014 Å). The europium ion in EuO is divalent, and in EuN it is trivalent. If these two compounds formed a simple solid solution, $EuN_{1-x}O_x$, one would expect (from Vegard's law) that, as the composition is changed from EuN to EuO, the lattice parameter would increase. This is the reverse of what is found for the SmN–$SmN_{1-x}O_x$ system; therefore, it is concluded that the samarium ions remain in the trivalent state as oxygen is exchanged for nitrogen.

Since samarium and gadolinium are known to form continuous-phase oxynitrides in which the substitution of oxygen for nitrogen decreases the nitride lattice parameter, it is natural to ask whether this is common for the other rare earths. There are probably exceptions to this, as EuN is thought to be, since EuO has a larger lattice parameter than EuN. Another exception might be YbN since ytterbium is more like europium than are any of the other rare earths. Although there are possible exceptions to the phenomenon, the exchange of oxygen for part of the nitrogen in rare earth nitrides to form a ternary phase may explain the questionable existence of LaO, NdO (see Figure 1), and YO, although no lattice parameter has been published for YO. This exchange may also explain the existence of CeO, despite the fact that CeO has a larger lattice parameter than CeN, since CeN (in which Ce has an oxidation state of $4+^{12}$) has an abnormally small lattice parameter compared to the other rare earth nitrides (see Figure 1).

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Solute–Solvent Interactions in Liquid Alloys from Cadmium Vapor Pressures over Dilute Solutions of Lead in Cadmium[1,2]

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Lead–cadmium solutions containing 0.004–0.032 mole fraction of lead have been studied at 777°K using an isopiestic balance. The measured cadmium vapor pressures over solutions in the composition range 0.004–0.01 mole fraction of lead may be described with a deviation not greater than 0.00015 activity unit (0.2 g-cal in the cadmium partial molal free energy) by the linear relationship $P_{\mathrm{Cd\ alloyed}}/P_{\mathrm{Cd\ pure}} = 1 - 1.63N_{\mathrm{Pb}}$, where P is the pressure over the alloy or over pure cadmium at the same temperature and N_{Pb} is the mole fraction of lead in solution. At larger concentrations curvature becomes observable, and from 0.015 to 0.032 mole fraction of lead the relationship $P_{\mathrm{Cd\ alloyed}}/P_{\mathrm{Cd\ pure}} = 1 - 2.04N_{\mathrm{Pb}} + 33.0N_{\mathrm{Pb}}^2$ is obeyed within 0.00034 activity unit, the cadmium activity becoming positive to Raoult's law at 0.9683 mole fraction of cadmium. This solvent behavior is tentatively interpreted as resulting from solute–solvent interactions which form complex species analogous in many respects to normal solvation reactions.

Vapor pressure measurements on some liquid metal solutions have demonstrated an unexpected complexity. Although the work was undertaken to test dilute solution theory, the complexity appears to be of considerable structural interest. This paper reports the lead–cadmium solution results; references to other published work are given in the Discussion section.

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstract H-73.

[3] Visiting Staff Member, Los Alamos Scientific Laboratory. Please send mail regarding this paper to Los Alamos.