[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

The Crystal Structure of Samarium Metal and of Samarium Monoxide[1]

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Samarium metal is found to be rhombohedral with unit cell dimensions of $a = 8.982 \pm 0.004$ Å. and $\alpha = 23.31 \pm 0.02°$. The unit cell contains three atoms giving a calculated density of $\rho = 7.52$ g. cm.$^{-3}$. The space group is R$\bar{3}$m (D_{3d}^5) and the atomic positions are: 1 Sm in (000), 2 Sm in $\pm (u,u,u)$ with $u = 0.222 \pm 0.003$. Each samarium atom has six ligands at 3.587 Å. and six at 3.629 Å., giving a mean metallic radius of 1.804 Å. The structure is close-packed, the period along the threefold axis being nine times the separation of consecutive close-packed layers. The sequence of layers is [ABABCBCAC]A···. The observed interatomic distances show that samarium has to be assigned three valence electrons. By heat treatment of samarium metal a coating of the monoxide is formed. SmO has the sodium chloride type of structure with $a_0 = 5.015$–5.050 Å., the reason for the variation in the unit-cell edge being uncertain.

E. I. Onstott[4] has described the preparation and some of the properties of samarium metal. The results of X-ray diffraction studies of Onstott's preparations are given in the present article.

Interpretation of the X-Ray Data

Table I gives the diffraction data as obtained with a small sliver of metal. The diffraction data of Table II were obtained with a similar sliver which had been heated to 625° for 15 min. in an evacuated vitreous silica capillary in an attempt to induce sharpening of the lines in the back-reflection region. Both tables cover the range up to $\sin^2 \theta = 0.518$ and Table II includes the back-reflection region as well. The diffraction pattern of the heat treated sample contains the lines of a second phase which is cubic face-centered with $a = 5.026 \pm 0.002$ Å. and which is believed to be SmO. Apart from these extra lines the two diffraction patterns are the same except for marked intensity differences which may be attributed to preferential orientation of the crystallites in the slivers.

The diffraction lines of samarium metal correspond to a rhombohedral unit cell of the following dimensions: $a = 8.982 \pm 0.04$ Å., $\alpha = 23.31 \pm 0.02°$. The corresponding hexagonal cell has dimensions: $a_1 = 3.629 \pm 0.002$ Å., $a_3 = 26.20 \pm 0.01$ Å.

Onstott's measured density of $\rho = 7.50$ g. cm.$^{-3}$ corresponds to three atoms in the rhombohedral cell, the calculated density being 7.52 ± 0.01 g. cm.$^{-3}$.

In a recent note[5] Daane, *et al.*, reported samarium metal to be rhombohedral with $a \cong 8$ Å. and $\alpha \cong 23.5°$, but give no further structural information.

It is immediately apparent from the diffraction data that the structure factor depends only upon the sum of the rhombohedral indices (*i.e.*, upon the third hexagonal index L). Accordingly the samarium atoms must lie on the threefold axis. If the presence of an inversion center is assumed, the only possible structure corresponds to the space group R$\bar{3}$m (D_{3d}^5) with the following atomic positions: 1 Sm(I) in (0,0,0), 2 Sm(II) in $\pm(u,u,u)$.

The parameter value u is readily found by noting the intensity variation with the index L for reflections with hexagonal indices $10L$ and $11L$. In the sequence $11L$ the reflection is absent unless L is a multiple of nine, and hence $u = 1/9, 2/9 \cdots$ In the sequence $10L$ the reflections with high intensity are for L = 4, 5, 13, 14, 22, 23, 31 and 32 showing that $u = 2/9$. On the basis of careful intensity consideration one may set

$$u = 0.222 \pm 0.003$$

TABLE I

X-RAY DIFFRACTION DATA FOR SAMARIUM METAL

Radiation: CuKα

Observed		Indices				Observed		Indices			
Intensity	$\sin^2 \theta$	Hexagonal	Rhombohedral	Calcd. $\sin^2 \theta$	$(F/f)^2 p$	Intensity	$\sin^2 \theta$	Hexagonal	Rhombohedral	Calcd. $\sin^2 \theta$	$(F/f)^2 p$
w −	0.0620	101	100	0.0610	1.8	m	0.2515	119	432	0.2502	18.0
vvw	.0652	102	110	.0636	0.8			204	220	.2540	6.5
s	.0705	009	333	.0700	3.0	vw −	.2622	205	311	.2618	6.5
w	.0750	104	211	.0739	6.5	w +	.2808	0.0.18	666	.2800	3.0
w	.0828	105	221	.0817	6.5	vw	.3906	2.0.13	553	.3862	6.5
vvw	.1044	107	322	.1024	0.8	vw	.4103	2.0.14	644	.4096	6.5
vw −	.1161	108	332	.1154	1.8	vw	.4331	214	310	.4342	13.0
vw −	.1486	1.0.10	433	.1465	1.8	vw	.4426	215	320	.4420	13.0
vw −	.1654	1.0.11	443	.1647	0.8	m	.4618	1.1.18	765	.4620	18.0
w +	.1813	110	$10\bar{1}$	.1802	9.0	vw	.4783	1.0.22	877	.4784	6.5
w −	.2079	1.0.13	544	.2061	6.5	vw −	.4905	2.0.17	755	.4900	1.8
w −	.2317	1.0.14	554	.2295	6.5	vw	.5163	1.0.23	887	.5173	6.5

The final column in Table I gives the calculated values of the quantity $(F/f)^2 p$ where F is the structure factor, f the scattering power and p the multiplicity factor. This quantity may be taken as

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(3) University of Chicago, Chicago, Illinois, and Consultant to Los Alamos Scientific Laboratory.

(4) E. I. Onstott, THIS JOURNAL, **75**, 5128 (1953).

(5) A. H. Daane, D. H. Dennison and F. H. Spedding, *ibid.*, **75**, 2272 (1953).

TABLE II

X-RAY DIFFRACTION DATA FOR HEAT TREATED SAMPLE OF SAMARIUM METAL, CuKα RADIATION

Observed Intensity	Observed $\sin^2\theta$	ΣH_i^2	SmO $\sin^2\theta$	Sm indices Hexagonal	Sm indices Rhombohedral	Calcd. $\sin^2\theta$
w	0.0623			101	100	0.0610
vvw	.0650			102	110	.0636
s	.0710	3	0.0705	009	333	.0700
vw	.0748			104	211	.0739
w+	.0826			105	221	.0817
m−	.0945	4	.0940			
vvw	.1033			107	322	.1024
vw	.1164			108	332	.1154
w−	.1474			1.0.10	433	.1465
vw	.1652			1.0.11	443	.1647
vw−	.1820			110	$10\bar{1}$	.1802
m	.1885	8	.1879			
m−	.2072			1.0.13	544	.2061
m	.2303			1.0.14	554	.2295
w−	.2520			119	432	.2502
				204	220	.2540
m−	.2592	11	.2584	205	311	.2618
m	.2817	12	.2819	0.0.18	666	.2800
w−	.3108			1.0.17	665	.3099
vw−	.3279			2.0.10	442	.3266
vvw	.3452			2.0.11	533	.3448
w	.3746	16	.3758	1.0.19	766	.3721
w	0.3898			2.0.13	553	0.3862
w	.4112			2.0.14	644	.4096
vvw	.4242			211	$20\bar{1}$	.4213
vw	.4363			214	310	.4342
w	.4467	19	0.4463	215	320	.4420
m	.4614			1.1.18	765	.4602
w−	.4702	20	.4698			
w+	.4797			1.0.22	877	.4784
vw	.4928			2.0.17	755	.4900
w+	.5177			1.0.23	887	.5173
vw	.8023			315	410	.8023
s	.8103			1.1.27	10.9.8	.8102
ms	.8208	35	.8222	3.0.18	855, 774	.8205
w+	.8388			2.1.22	976	.8387
w+	.8445	36	.8456			
m−	.8780			2.1.23	986	.8776
s−	.8905			1.0.31	11.10.10	.8906
vw	.9177			2.0.28	10.10.8	.9178
vw	.9273			3.1.13	652	.9267
w	.9397	40	.9396			
s	.9450			1.0.32	11.11.10	.9450
ms	.9500			3.1.14	743	.9500

proportional to the intensity as long as only neighboring reflections are compared and provided there is no preferential orientation. In the sample upon which Table I is based there is a moderate amount of preferential orientation. This is shown by the enhanced observed intensity for reflections with high values of the ratio $L^2/(H^2 + HK + K^2)$, where HKL are the hexagonal indices. The degree of preferred orientation is much higher in the heat treated sample.

Because of the preferred orientation a direct comparison of observed intensities for the heat treated sample with calculated values of the quantity $(F/f)^2p$ should be made only for comparable values of the ratio $L^2/(H^2 + HK + K^2)$. To facilitate this comparison the observed intensities for reflections with hexagonal indices $10L$ and $11L$ are arranged in Table III according to increasing values of L. As a consequence of the preferred orientation the intensity comparison given in Table I should not be used to judge the validity of the structure.

TABLE III

DIFFRACTION INTENSITIES FOR HEAT TREATED SAMARIUM METAL SAMPLE

Reflections $10L$						Reflections IIL		
L	$(F/f)^2p$	Obsd. intensity	L	$(F/f)^2p$	Obsd. intensity	L	$(F/f)^2p$	Obsd. intensity
1	1.8	w	17	1.8	w−	0	9.0	vw−
2	0.8	vvw	19	1.8	w[a]	3	0.0	m[a]
4	6.5	vw	20	0.8	nil	6	0.0	nil
5	6.5	w+	22	6.5	w+	9	18.0	m
7	0.8	vvw	23	6.5	w+	12	0.0	nil
8	1.8	vw	25	0.8	vw	15	0.0	nil
10	1.8	w−	26	1.8	vw	18	18.0	m
11	0.8	w−	28	1.8	vw	21	0.0	nil
13	6.5	m−	29	0.8	vw	24	0.0	nil
14	6.5	m	31	6.5	s−	27	18.0	s
16	0.8	m[a]	32	6.5	s	30	0.0	nil

[a] Coincidence with SmO line.

Discussion of the Structure

The structure can be described as consisting of close-packed hexagonal layers normal to the threefold axis. With the parameter $u = 2/9$ these layers are equidistantly spaced, the period along the threefold axis being nine times the layer separation. The type of stacking of the layers may be described by the sequence [ABABCBCAC]AB · · · · ·, the bracket representing the repetitive unit.

Each samarium atom has six ligands in the same hexagonal layer at a distance of 3.629 Å., and six additional ligands at 3.587 Å., three in the adjacent layer above and three in the layer below. The latter six ligands form a trigonal antiprism about Sm(I) and a trigonal prism about Sm(II). Thus, the immediate neighborhood of a Sm(I) atom is the same as for cubic close-packing, while that of a Sm(II) atom is the same as for simple hexagonal close-packing.

The metallic radius of samarium is compared with that of the other 4f-elements in Table IV. The observed value of 1.804 Å. for the samarium radius lies on the smooth curve connecting the radii of the typically trivalent 4f-elements. Hence, one is led to conclude that there are $V = 3.0$ valence electrons

TABLE IV

METALLIC RADII OF THE 4f-ELEMENTS[a]

Element	Radius, Å.	V	Element	Radius, Å.	V
La	1.871	3.0	Tb	1.773	3.1
Ce	1.818	3.2	Dy	1.770	3.0
Pr	1.824	3.1	Ho	1.761	3.0
Nd	1.818	3.0	Er	1.748	3.0
Pm	...		Tm	1.743	3.0
Sm	1.804	3.0	Yb	1.933	2.0
Eu	2.084	2.0	Lu	1.738	3.0
Gd	1.795	3.0			

[a] Values for radii of elements other than samarium are taken from L. Pauling, THIS JOURNAL, 69, 542 (1947).

per atom in samarium metal. In view of the considerable stability of divalent samarium compounds a value slightly less than 3.0 for the number of valence electrons, *V*, in the metal might have been anticipated.

The Crystal Structure of Samarium Monoxide

The diffraction data in Table II show the presence of a cubic face-centered phase with $a = 5.026 \pm 0.002$ Å. in the heat treated sample of samarium metal. From the method of preparation this phase may be expected to be an oxide and it is reasonable to identify the phase with the grey coating formed on metal pieces on heat treatment. The phase has been observed in a number of samples. Indeed, one particular sample, resulting from an attempt to reduce samarium bromide with lithium metal, gave only the the diffraction lines of this cubic phase. The measurements of this pattern are listed in Table V.

TABLE V

DIFFRACTION DATA FOR SAMARIUM MONOXIDE

Radiation: CuKα

Sin² θ Obsd.	Sin² θ Calcd.	ΣH_i^2	Intensity Obsd.	Intensity Calcd.
0.0710	0.0698	3	100	110
.0944	.0931	4	70	86
.1882	.1861	8	70	59
.2583	.2560	11	100	50
.2815	.2793	12	35	20
.3759	.3724	16	20	9
.4448	.4422	19	50	19
.4678	.4655	20	70	26
.5608	.5586	24	50	21
.6309	.6284	27	60	20
.7466	.7448	32	30	11
.8152	.8147	35	80	38
.8383	.8379	36	80	35
.9310	.9310	40	80	40

The reflections with even values of ΣH_i^2 are appreciably stronger relative to those with odd values of ΣH_i^2 than can be accounted for by the samarium atoms alone. One is led to conclude that the cubic phase is SmO with the sodium chloride type of structure. The last column of Table V gives the intensities calculated on this basis with the aid of the formula

$$I \propto |F|^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

The unit-cell constant is observed to vary from sample to sample, the lowest observed value being $a = 5.015 \pm 0.002$ Å. and the highest $a = 5.050 \pm 0.002$ Å. It is not known whether the variation is caused by impurities or by deviations from the ideal composition SmO.

The interatomic distance of Sm–6O = 2.52 Å. is about 0.06 Å. smaller than calculated from the ionic radii.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, AND THE RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Stability of the Lower Oxidation States of Indium in Aqueous Solution

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The equilibria between In^{+3}(aq) and In(m) have been investigated. Equilibrium constants for the reactions: $2In(m) + In^{+3}(aq) = 3In^{+}(aq)$ and $In(m) + 2In^{+3}(aq) = 3In^{+2}(aq)$ have been determined to be 2.4×10^{-11} and 1.9×10^{-8}, respectively. From these results the standard potentials are calculated: $In(m) = In^{+}(aq) + e^{-}$, $E^0 = 0.14$; $In^{+}(aq) = In^{++}(aq) + e^{-}$, $E^0 = 0.40$; $In^{++}(aq) = In^{+3}(aq) + e^{-}$, $E^0 = 0.49$.

Introduction

It has long been known that such compounds as $InCl$ and $InCl_2$ or In_2Cl_4 exist. Thiel[1] has observed that if one reacts either of the lower oxidation state chlorides with water, one obtains a solution containing tripositive indium ions and a deposit of indium metal. All of this information leads one to expect such species as In^{+} and In^{++} may exist in aqueous solution at low concentration even though they are unstable at high concentrations with respect to disproportionation to the metal and the In^{+3}(aq) ion.

To account for the observations of Thiel, Latimer[2] has taken the approximate potentials for the various indium couples to be

$$In = In^{+} + e^{-} \qquad E^0 = ca.\ 0.25 \qquad (1)$$

$$In^{+} = In^{++} + e^{-} \qquad E^0 = ca.\ 0.35 \qquad (2)$$

$$In^{++} = In^{+3} + e^{-} \qquad E^0 = ca.\ 0.45 \qquad (3)$$

There are a number of reasons for choosing these approximate potentials. The sum of the three potentials must be 3 × 0.340 (where 0.340 is the In–In^{+3} potential). In order to account for the observed decompositions, the potential for couple 3 must be greater than that for couple 2 and similarly, the potential for couple 2 must be greater than that for couple 1.

Latimer[2] also has made an approximate calculation of the potential of couple 1. The entropy of $InCl(c)$ was estimated to be 23.2 in comparison to 23.0 for $AgCl$. This leads to a value for the entropy of formation of $InCl(c)$ which may be combined with the Bureau of Standards[3] value for the heat to

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(1) A. Thiel, *Z. anorg. Chem.*, **39**, 119 (1904); **40**, 280 (1904).

(2) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Second Edition, Prentice-Hall Inc., New York, N. Y., 1952.

(3) National Bureau of Standards, Circular 500 (Feb., 1952), "Selected Values of Chemical Thermodynamic Properties."