Table I

X-Ray Data for CrOOH (III)

Orthorhombic indices *hkl*	*I* obsd.	*d* obsd., Å.	*d* calcd., Å.
110	s	3.214	3.217
101	m−	2.522	2.528
011 200	m+	2.429	2.437 2.431
111	m−	2.174	2.178
020	w−	2.145	2.146
210	m−	2.112	2.115
211	m	1.720	1.721
121	m+	1.636	1.636
220	m−	1.608	1.609
310	w	1.515	1.516
002	w	1.478	1.480
301	m−	1.421	1.421
130	w	1.373	1.372
112	m−	1.343	1.345
031	w	1.288	1.288
202	w	1.263	1.264
131	w	1.245	1.245
230	w	1.233	1.233
212 400	w	1.212	1.213 1.215
122 321	w	1.185	1.182 1.185

by examining differences of $\sin^2 \theta$ values. The unit cell was corroborated by electron diffraction data.

An approximate mean refractive index of 1.9 was determined microscopically by the immersion method. The material was light yellow-green in transmission, but was too finely divided for any individual crystal to be distinguished. Individual crystals as observed in the electron microscope had no recognizable outline, although they were shown to be single by selected area electron diffraction.

An identical product III was obtained by similar treatment of CrO_2 in 3 *M* NaOH or 0.25 *M* $K_2Cr_2O_7$ solutions, instead of water.

Heating of III at 110° in air caused no loss in weight. Ignition at 1000° yielded Cr_2O_3, with a weight loss of 11.05%. No foreign lines were detected in the X-ray powder diffraction pattern of the Cr_2O_3, using Cr Kα radiation. The weight loss was shown to represent H_2O by direct collection and weighing. A weighed sample of III was sealed in an evacuated fused silica tube fitted with a small-bore side arm. The side arm was cooled with Dry Ice, and the sample was heated to red heat with a hydrogen torch. Water was seen to condense in the side arm and was ultimately caused to accumulate at the end of the side arm, which was then sealed off and separated from the main tube. The tube containing the collected water was allowed to reach room temperature, and a small opening was made by breaking off the pointed end of the glass. The tube was immediately weighed. It was then heated at 110° and reweighed. The weight loss corresponding to the collected water was 11.11% of the sample weight. The weight loss calculated for the reaction $2CrOOH \rightarrow Cr_2O_3 + H_2O$ is 10.59%. The empirical formula of III is therefore assumed to be CrOOH.

Samples of I and III were placed in unsealed envelopes of platinum foil and heated simultaneously at 335° in air in a tube furnace. After 6 hr., X-ray diffraction showed that III had converted completely to CrO_2, whereas I showed only partial conversion. After a further 72 hr., III still yielded only CrO_2, but I gave a mixture of CrO_2 and Cr_2O_3. More prolonged heating, for a total of 225 hr. at 335°, produced no further change in either sample.

Discussion

Treatment of CrO_2 in water at temperatures near 450° yields a green compound of empirical formula CrOOH. This appears to be a new phase modification of CrOOH, of orthorhombic structure, in contrast to the previously reported red, rhombohedral form. Direct interconversion of the two forms has not been observed. Heating of the green, orthorhombic form in air at about 350° causes complete and ready conversion to CrO_2, which is stable under these conditions. Similar heating of the red, rhombohedral form causes a slower conversion to CrO_2, mixed with some Cr_2O_3. The Cr_2O_3 content does not increase once all the CrOOH has been decomposed. This difference in behavior may be explained by the physical form of the green, orthorhombic CrOOH, which was much more finely divided and would be expected to oxidize more readily during decomposition, thereby avoiding the formation of unreactive aggregates of Cr_2O_3. Somewhat similar behavior is also found in the oxides and oxyhydroxides of iron. The following reversible reaction has thus been demonstrated for the green, orthorhombic CrOOH

$$2CrO_2 + H_2O \underset{350^\circ \text{ in air}}{\overset{450^\circ \text{ under pressure}}{\rightleftarrows}} 2CrOOH + (1/2)O_2 \qquad (1)$$

This reaction appears to be the first reported route to synthesis of pure CrO_2 under atmospheric conditions,[1] although it is necessary to use hydrothermal conditions to prepare the intermediate green, orthorhombic CrOOH.

Formation of the red, rhombohedral CrOOH has been considered[7] in terms of a reaction between protons and polymeric Cr^{VI} ions $(HCrO_4)_n^{-n}$

$$nH^+ + (HCrO_4)_n^{-n} = nCrOOH + (3n/4)O_2 + (n/2)H_2O \qquad (2)$$

In contrast, the green, orthorhombic CrOOH now reported appears to result from direct hydrolysis of CrO_2, according to eq. 1.

Acknowledgments.—This work arose out of a study of CrO_2 suggested by Dr. D. Chapin, M.I.T., Lincoln Laboratory, whose interest and encouragement are appreciated. Thanks are due to J. J. Comer and R. H. Curry for electron diffraction and emission spectrographic measurements.

Contribution from Tem-Pres Research, Inc.,
State College, Pennsylvania

Samarium and Lanthanum Tungstates of the $3R_2O_3 \cdot WO_3$ Type

By Luke L. Y. Chang and Bert Phillips

Received June 5, 1964

In the course of a recent investigation, four stable phases were found along the Sm_2O_3–WO_3 join[1] in the system Sm–W–O. The Sm_2O_3:WO_3 ratios for these phases are 1:3, 1:1, 7:4, and 3:1. Among the five

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(1) B. Phillips, L. L. Y. Chang, and M. G. Scroger, to be published.

TABLE I

X-RAY DATA FROM POWDERS OF DISORDERED PYROCHLORE, ORDERED PYROCHLORE, AND FLUORITE

	Disordered pyrochlore (ordered defect fluoride)				Ordered pyrochlore[a]			Fluorite[b]	
	$3Sm_2O_3 \cdot WO_3$		$3La_2O_3 \cdot WO_3$		$Sm_2O_3 \cdot 2TiO_2$			CaF_2	
hkl	*d*-spacing, Å.	Rel. intensity	*d*-spacing, Å.	Rel. intensity	*d*-spacing, Å.	Rel. intensity	*hkl*	*d*-spacing, Å.	Rel. intensity
111					5.91	22			
200	5.62	1	5.73	10					
311					3.09	22			
222	3.123	100	3.228	100	2.96	100	111	3.153	94
400	2.709	40	2.793	43	2.56	60			
331					2.35	36			
422	2.206	2	2.281	4	2.076	4			
511/333					1.969	14			
440	1.910	65	1.978	59	1.809	68	220	1.931	100
531					1.730	11			
533					1.560	6			
622	1.629	55	1.685	53	1.543	41	311	1.647	35
444	1.559	16	1.613	18	1.477	17	222	1.577	2
711/551					1.432	6			
731/553					1.332	8			
800	1.352	10	1.397	10	1.229	9	400	1.366	12
733					1.250	4			
751/555					1.182	6			
662	1.239	21	1.282	23	1.174	18	331	1.253	10
840	1.208	16	1.249	18	1.144	19			
911/753					1.123	8			
931					1.073	15			
844	1.103	15	1.141	15	1.044	15	422	1.1150	16
933/771/775					1.028	7			
10.2.0/862					1.003	5			
951/773					1.9895	5			
10.2.2/666	1.039	12	1.076	14	1.9841	16	511/333	1.0512	7
880	0.9548	4	0.9883	5	0.9041	13	440	0.9651	5
11.3.1/971/955					0.8938	6			
11.3.3/973					0.8676	5			
10.6.2	0.9130	8	0.9449	8	0.8544	13	531	0.9233	7

[a] R. S. Roth, *J. Res. Natl. Bur. Std.*, **52,** 17 (1956). [b] H. E. Swanson and E. Tatze, National Bureau of Standards Circular 5-39, U. S. Government Printing Office, Washington, D. C., 1953, p. 69.

yttrium–tungsten oxides reported by Borchardt,[2] three of these ratios are found but he reports a 15:8 instead of a 7:4 composition. His later work contains data on rare earth–tungsten oxides with R_2O_3:WO_3 ratios of 1:1 and 1:3 only.[3] The isotropy and the refractoriness of the $3Sm_2O_3 \cdot WO_3$ phase which we prepared prompted the preparation of the lanthanum analog and a study of the possible solid solution series between these two compounds.

All compositions were prepared by solid-state reaction of the oxides at or above 1400°. Samples were sealed in platinum capsules in air to prevent volatilization of WO_3 which would change the total composition, although the phases could be prepared at 1400° without encapsulation. Reaction was complete at 1400 and 1600° after 6 and 0.5 hr., respectively. The capsules were quenched in air and the samples were examined by microscopy and X-ray diffraction.

The compound $3Sm_2O_3 \cdot WO_3$, which has a light yellow color, is a very refractory material with a congruent melting point of 2240 ± 20°. The $3La_2O_3 \cdot WO_3$ compound, which is white, is also very refractory, melting at 2050 ± 20°. Differential thermal analysis to 1400° showed no heat effect in either compound.

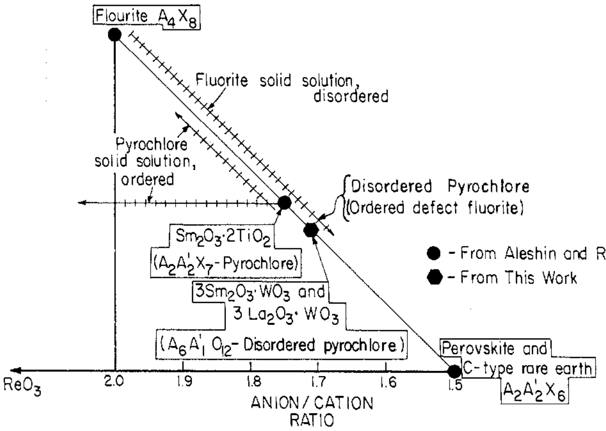

Fig. 1.—Chart illustrating compositional and structural relations among fluorite, pyrochlore, and perovskite structures (after Aleshin and Roy[4]) and the disordered pyrochlore prepared in this work.

Both compounds lose oxygen when heated above 800° under vacuum without change in structure but with color changes toward gray. Reheating in air restores the original color. Intermediate compositions formed single-phase products with intermediate colors.

The crystallographic properties were determined from X-ray powder diffraction patterns. The patterns

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(2) H. J. Borchardt, *Inorg. Chem.*, **2,** 170 (1963).

(3) H. J. Borchardt, *J. Chem. Phys.*, **39,** 504 (1963).

(4) E. Aleshin and R. Roy, *J. Am. Ceram. Soc.*, **45,** 18 (1962).

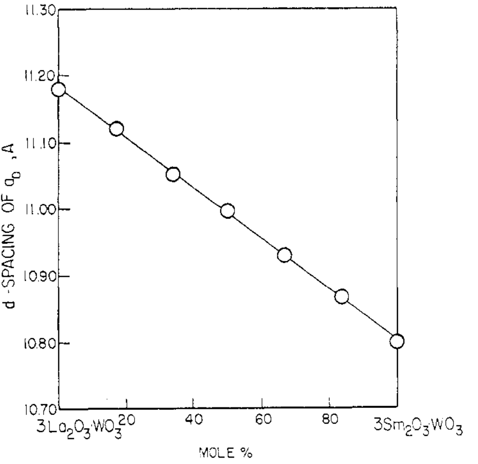

Fig. 2.—Diagram illustrating values of a_0 for compositions in the $3(La_xSm_{2-x}O_3) \cdot WO_3$ series.

are simple and can be indexed easily as those of a face-centered cubic unit cell. By comparison with several common known structural types of mixed oxides, both compounds have a similar structure and can be classed as disordered pyrochlore (or ordered defect fluorite[4]) with a_0 = 10.80 Å. for $3Sm_2O_3 \cdot WO_3$ and a_0 = 11.18 Å. for $3La_2O_3 \cdot WO_3$. The X-ray powder data of and the composition–structure relations among the two compounds, an ordered pyrochlore and fluorite, are presented in Table I and Fig. 1.[5] The presence of specific reflections in the patterns of the tungstates, *e.g.*, the 200 and 422 in $3La_2O_3 \cdot WO_3$, requires the use of pyrochlore cell sizes. Reducing the *hkl* values to correspond to a fluorite cell results in odd–even combinations which are prohibited in face-centered cubic lattices.

The disordering of both $3Sm_2O_3 \cdot WO_3$ and $3La_2O_3 \cdot WO_3$ is shown by the absence of the three distinct ordering reflections (111), (331), and (531) which exist for ordered pyrochlore. The intensity of the reflection (200) of a disordered pyrochlore is found to be a function of composition in the $3(La_xSm_{2-x}O_3) \cdot WO_3$ series. The more samarium contained, the lower is the intensity of the reflection (200), and it can be barely detected in the $3Sm_2O_3 \cdot WO_3$ phase, indicating a decrease in order with an increase in samarium content. Attempts to develop ordering of the type that exists in an ordered pyrochlore by heat treatment at 800 and 1000° for 4 days were unsuccessful.

Plotting the nominal values of a_0 calculated from the last seven diffraction lines of the disordered pyrochlore structure against composition in the $3(La_xSm_{2-x}O_3) \cdot WO_3$ series shows a close correlation with Vegard's law (Fig. 2). This could be expected in view of the similarity of lanthanum and samarium.

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(5) It deserves mention that by coincidence the *d*-spacing values and relative intensities of the $3Sm_2O_3 \cdot WO_3$ end member prepared in this study are similar to those reported for the zinc blende form of ZnS. The mixed oxide, cannot, of course, be of the zinc blende type, but the similarity is deceiving and therefore noteworthy.

CONTRIBUTION FROM THE CENTRAL BASIC
RESEARCH LABORATORY, ESSO RESEARCH AND
ENGINEERING CO., LINDEN, NEW JERSEY

Tricarbonyl(condensed aromatic)iron(0) Complexes

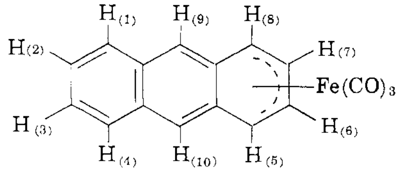
BY T. A. MANUEL

Received June 22, 1964

Benzene and its simple substitution products have not been reported to form isolable iron carbonyl complexes. However, extended conjugation appears to permit the π-electrons of a benzene ring to participate in bonding to iron carbonyl groups, as has been demonstrated in the cases of hexacarbonyl(*m*- or *p*-divinylbenzene)diiron[1] and hexacarbonyl(acenaphthalene)diiron.[2] The compounds tricarbonyl(naphthalene)iron and tricarbonyl(anthracene)iron have been briefly described,[3] the former being identified only by infrared analysis. Seeking to learn more about these two compounds and about the extent of conjugation needed to permit complex formation between aromatics and iron tricarbonyl groups, we have investigated the reactions between iron carbonyls and naphthalene, anthracene, 1-vinylnaphthalene, and 9-acetylanthracene.

Among the products of the treatment of naphthalene with pentacarbonyliron or dodecacarbonyltriiron we have found evidence of only one iron carbonyl complex, isolated only in trace amounts, and in less than analytical purity. This material has been shown to contain appreciable amounts of sulfur, and its infrared and n.m.r. spectra identify it as hexacarbonyl(thianaphthene)diiron.[4] This compound may well be identical with Harper's "naphthalene-iron tricarbonyl."[3]

We have also obtained the tricarbonyl(anthracene)iron reported by Harper.[3] The n.m.r. spectrum (Table I) of the slightly soluble compound is consistent with structure I, in which the iron atom is bonded to a terminal ring. For comparison we include the n.m.r.



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(1) T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3597 (1961).

(2) R. B. King and F. G. A. Stone, *ibid.*, **82**, 4557 (1960).

(3) R. J. Harper, U. S. Patent 3,073,855 (Jan. 15, 1963) (assigned to the Ethyl Corporation).

(4) R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).