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Crystallographic Studies of Perovskite-Like Compounds. I. Rare Earth Orthoferrites and $YFeO_3$, $YCrO_3$, $YAlO_3$

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The orthoferrites of the trivalent ions Gd, Eu, Sm, Nd, Pr, La, and Y and the compounds $YCrO_3$ and $YAlO_3$ are isostructural. They belong to space group D_{2h}^{16}–*Pbnm* with four distorted perovskite units in the true crystallographic cell. X-ray and morphological data on these crystals are given and the relationships among them are discussed.

Introduction

Much X-ray work has been done on compounds with distorted perovskite structures, but, because it has for the most part been done on powders, it has not been definitive in all cases. Recently, J. P. Remeika (1956) of these Laboratories has succeeded in preparing single crystals (of size suitable for X-ray and optical examination) of a considerable number of compounds with general formula ABO_3 which are perovskite-like. One of these compounds is gadolinium orthoferrite, $GdFeO_3$, the crystal structure of which has been worked out in some detail (Geller, 1956) from single crystal X-ray data. It was found that the structure consists of four distorted perovskite pseudo-cells in an orthorhombic cell, the most probable space group being D_{2h}^{16}–*Pbnm*.*

The magnetic properties of the orthoferrite powders have been extensively investigated by Néel and his school (Néel, 1954; Pauthenet & Blum, 1954; Guiot-Guillain, 1953). Gilleo (1956*a*, *b*) has studied the magnetic properties of a crystal of $GdFeO_3$, and the magnetic structure of $LaFeO_3$ has been studied with neutrons by Roth (1954).

The work described herein deals with eight compounds isomorphous with $GdFeO_3$: the orthoferrites of Pr, Nd, Sm, Eu, La and Y; $YAlO_3$ and $YCrO_3$.

Crystallographic data on the perovskite-like compounds

The structure of $GdFeO_3$ was determined mainly from intensities obtained from Buerger precession camera photography of a ground plate crystal (see Geller, 1956). Single-crystal photographs (both Weissenberg and precession) were taken of $LaFeO_3$ and $YFeO_3$ crystals, using Mo *K* radiation. Powder photographs were taken of all the compounds with Cr *K* radiation.

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* See, however, the reservation in the Geller (1956) reference.

Table 1. *Powder diffraction data for* $GdFeO_3$ *and isomorphs*

INDEX	$GdFeO_3$			$EuFeO_3$			$SmFeO_3$		
	$d_{(Obs)}$	$d_{(Calc)}$	I	$d_{(Obs)}$	$d_{(Calc)}$	I	$d_{(Obs)}$	$d_{(Calc)}$	I.
110	3.880	3.872	M-S	3.864	3.880	M-S	3.874	3.882	M-S
002	3.831	3.834	VW	3.837	3.843	VW	3.841	3.856	VW
111	3.461	3.456	S	3.457	3.463	M-S	3.466	3.467	M-S
020	2.810	2.808	M-S	2.800	2.806	M	2.794	2.796	M
112	2.725	2.724	VS	2.726	2.730	VS	2.736	2.736	VS
200	2.677	2.673	M-S	2.675	2.685	M	2.695	2.697	M
021	2.636	2.637	M	2.637	2.635	W-M	2.629	2.629	M
103	2.304	2.305)	W	2.305	2.312)	W	2.316	2.320)	W
211		2.302)			2.310)			2.317)	
022	2.268	2.265	W-M	2.260	2.266	W-M	2.260	2.263	W-M
202	2.200	2.193	M	2.199	2.201	M	2.211	2.210	M
113	2.134	2.133	M	2.129	2.138	M	2.137	2.143	M
122	2.083	2.086	VW	2.084	2.088	VW			
220	1.936	1.936	M-S	1.937	1.940	MS	1.942	1.941	M-S
004	1.916	1.917	W-M	1.922	1.922	W-M	1.925	1.928	M
023	1.890	1.890	M	1.889	1.892	M	1.884	1.892)	M-S
221	1.877	1.877	M	1.877	1.881	M		1.882)	
213	1.757	1.755	VW-W	1.760	1.760	W	1.760	1.766)	VW
301	1.741	1.736	VW					1.751)	
114	1.720	1.718)	S	1.720	1.721)	S	1.721	1.727)	S
131		1.722)			1.721)			1.718)	
310	1.700	1.699	VW	1.712	1.706	VW	1.704	1.712	VW
311	1.659	1.658	W	1.664	1.665	W	1.672	1.671	VW-W
132	1.604	1.605	M	1.603	1.605	M	1.603	1.602	M-S
024	1.583	1.583	M	1.584	1.585	M	1.588	1.587	M
204	1.558	1.558	VW-W	1.559	1.563)	S-VS	1.566	1.568)	S-VS
312	1.553	1.553	S-VS		1.559)			1.564)	
105									
231									
303									
321									
320									
223	1.544	1.543	W-M	1.545	1.547	W-M	1.550	1.549	W-M
133	1.453	1.453	M-S	1.453	1.454	M-S	1.454	1.453	M-S
115	1.426	1.426	VW-W	1.429	1.429	VW	1.434	1.433	VVW
313	1.416	1.415	VW	1.420	1.420	VVW	1.427	1.425	VVW
040				1.401	1.403	W	1.400	1.398	VW-W
041	1.380	1.381	W-M	1.379	1.380	M	1.377	1.376	W-M
224	1.362	1.362	M-S	1.364	1.365	M-S	1.368	1.368	M-S
025	1.346	1.346	W		1.348	ov.(400)	1.350	1.356	VW
140									
400	1.337	1.337	W-M	1.342	1.343	W-M	1.349	1.349	W-M
215				1.297	1.298)	VW	1.302	1.302)	VVW
323					1.300)			1.303)	
233				1.316	1.317)	VW			
042					1.318)				
125				1.306	1.307)	VVW			
410					1.306)				
142	1.282	1.280)	VW-W		1.280	ov.(006)		1.277	ov.(331)
411		1.282)		1.288	1.287	W	1.295	1.292)	VW
330								1.294)	
134					1.300	ov.(215)			
006		1.278	ov.(411)	1.281	1.281	VW-W	1.285	1.285	W
314	1.272	1.271)	M-S	1.276	1.276)	M-S		1.280)	
331		1.273)			1.275)		1.278	1.276)	W-M
402	1.266	1.262	VW-W	1.268	1.268	VW		1.273)	
043								1.228	ov.(332)
240				1.243	1.243	VW	1.242	1.241)	VW-W
412	1.230	1.231	VW-W	1.230	1.236	VW-W		1.241)	
241	1.226	1.227	M-S	1.227	1.227	M-S	1.227	1.225	M-S
332	1.223	1.223	W-M	1.225	1.226	M-S	1.228	1.227	M-S
116	1.214	1.214	S	1.216	1.216	S	1.220	1.220	S
420	1.207	1.207	W-M	1.211	1.211	M	1.217	1.215	M-S
225	1.202	1.202)	W-M	1.205	1.205	M-S	1.208	1.207	W-M
143		1.199)		1.197	1.197)	M	1.201	1.197)	W
234					1.199)			1.200)	
421	1.192	1.192	W-M		1.196)			1.200)	
324	1.184	1.184	VW	1.186	1.187	VW	1.192	1.190	VW-W
242	1.182	1.182	VW-W	1.183	1.183	VW-W	1.183	1.181	VVW
026	1.163	1.163	VW-W	1.165	1.165	VW	1.169	1.168)	VW-W
413	1.159	1.159	VW-W	1.163	1.163	W-M		1.168)	
305					1.166	ov.(026)		1.170)	
135	1.158	1.158	S	1.159	1.159	S	1.161	1.160)	S
206	1.153	1.153	VW-W	1.157	1.156	W-M		1.160)	
422				1.154	1.155)	S-VS	1.157	1.158)	M-S
333	1.152	1.152	S		1.155)			1.156)	
315									

INDEX	$NdFeO_3$			$PrFeO_3$			$LaFeO_3$		
	$d_{(Obs)}$	$d_{(Calc)}$	I	$d_{(Obs)}$	$d_{(Calc)}$	I	$d_{(Obs)}$	$d_{(Calc)}$	I
110	3.894	3.893	M-S	3.896	3.915)	M-S	3.929	3.932)	M
002	3.867	3.876	VW		3.904)			3.931)	
111	3.482	3.479	M-S	3.485	3.499	M	3.514	3.517	W-M
020	2.783	2.787	M-S	2.790	2.789	M-S	2.778	2.782)	VS
112	2.746	2.746	VS	2.755	2.765	VS		2.780)	
200	2.725	2.720	M	2.750	2.747	M		2.778)	
021	2.624	2.622	W-M	2.618	2.627	W-M	2.622	2.623	W
103	2.328	2.334)	W-M	2.344	2.353)	W	2.368	2.370)	W-M
211		2.331)			2.350)			2.370)	
022	2.265	2.263	M	2.264	2.270	M	2.269	2.271)	M-S
202	2.224	2.227	M	2.244	2.247	M		2.269)	
113	2.154	2.153	W-M	2.163	2.168	W	2.178	2.181	VW-W
122	2.085	2.089	W				2.100	2.102	VW
220	1.946	1.946	M-S	1.956	1.957	S	1.965	1.966)	S
004	1.933	1.938	W-M	1.950	1.953	M		1.966)	
023	1.890	1.897)	M-S	1.897	1.903)	M	1.908	1.908)	W-M
221		1.888)			1.899)			1.907)	
213							1.803	1.803)	VW-W
301								1.803)	
114	1.734	1.735	M	1.745	1.747	M	1.757	1.758	M
131	1.716	1.715	M-S	1.716	1.718	M-S	1.717	1.717	M
310		1.725	ov.(114)		1.740	ov.(114)			
311	1.685	1.683	W-M	1.697	1.699	W		1.715	ov.(131)
132	1.602	1.601	M-S	1.605	1.605	M-S	1.603	1.606)	S-VS
024	1.589	1.591	M	1.597	1.599	M		1.605)	
204	1:576	1.579)	S-VS	1.589	1.592)	S-VS		1.605)	
312		1.576)			1.589)			1.604)	
105							1.513	1.513)	VW
231								1.514)	
303								1.512)	
321								1.513)	
320									
223	1.555	1.554	W-M	1.563	1.564	W			
133	1.454	1.454	M-S	1.459	1.459	M	1.460	1.461)	W
115								1.460)	
313								1.459)	
040	1.394	1.393	W	1.394	1.395	W	1.391	1.391	W
041	1.374	1.371)	S-VS	1.372	1.373	M	1.370	1.370	W
224		1.373)		1.382	1.382	S-VS	1.389	1.390	S
025		1.359	ov.(400)	1.360	1.363	VVW		1.369	ov.(041)
140									
400	1.361	1.360	W-M	1.375	1.374	M		1.389	ov.(224)
215								1.329)	
323								1.329)	ov.(411)
233								1.329)	
042								1.311	ov.(006)
125	1.321	1.321	VW					1.329	ov.(411)
410									
142									
411	1.304	1.303	W				1.328	1.328	W
330							1.310	1.310)	W-M
134		1.302	ov.(411)	1.299	1.308)	W-M		1.311)	
006	1.292	1.292)	W-M		1.302)			1.310)	
314		1.291)			1.299)			1.310)	
331	1.281	1.280)	M-S	1.288	1.287	W-M	1.291	1.293	W
402		1.283)			1.296	ov.(006)		1.310	ov.(006)
043		1.226	ov.(116)		1.229	ov.(241)		1.229	ov.(225)
240	1.243	1.239	W-M	1.243	1.243	W		1.244	ov.(116)
412									
241	1.224	1.224	M-S	1.228	1.228	M		1.229	ov.(225)
332	1.232	1.231	M-S	1.238	1.238	M-S	1.242	1.243)	S
116	1.226	1.226	S-VS	1.235	1.235	S		1.243)	
420		1.222	ov.(241)	1.232	1.232	M-S		1.243)	
225	1.213	1.213	M	1.220	1.221	W-M	1.229	1.228	W-M
143									
234									
421	1.208	1.207	W-M	1.218	1.217	W-M	1.227	1.227	W
324									
242				1.187	1.185	VW	1.184	1.186)	W-M
026	1.172	1.172	W-M	1.178	1.180	W		1.185)	
413	1.177	1.176)	W-M		1.187)				
305		1.178)			1.187)	ov.(242)			
135	1.164	1.163	S	1.168	1.169	M-S		1.172	ov.(333)
206	1.167	1.167)	M	1.176	1.176	W-M		1.185)	ov.026
422		1.166)						1.185)	
333	1.161	1.160	S	1.166	1.167	S	1.172	1.172)	M-S
315	1.153	1.153	VW-W	1.162	1.162	W		1.172)	

INDEX	$YFeO_3$			$YCrO_3$			$YAlO_3$		
	$d_{(Obs)}$	$d_{(Calc)}$	I	$d_{(Obs)}$	$d_{(Calc)}$	I	$d_{(Obs)}$	$d_{(Calc)}$	I
110	3.841	3.847	M	3.779	3.802	W-M	3.693	3.714	M
002	3.799	3.811	VW	3.740	3.770	VW	3.668	3.685	VW
111	3.432	3.434	S	3.374	3.395	M	3.306	3.317	M
020	2.794	2.755	M-S	2.752	2.759	W-M	2.656	2.665	W-M
112	2.705	2.707	VS	2.661	2.667	VS	2.611	2.616	VS
200	2.651	2.651	M	2.614	2.623	W	2.584	2.590	W
021	2.627	2.624	M	2.581	2.591	W-M	2.498	2.506	W-M
103	2.285	2.291)	W-M	2.251	2.267)	M	2.217	2.220)	W-M
211		2.281)			2.251)			2.221)	
022	2.254	2.254	W-M	2.218	2.227	W	2.155	2.159	M
202	2.174	2.176	W-M	2.144	2.153	W-M	2.112	2.119	M
113	2.120	2.117	M	2.086	2.097	M	2.044	2.050	W
122	2.073	2.074	VW				1.988	1.993	VW
220	1.923	1.923	M-S	1.897	1.901	M-S	1.854	1.857	S
004	1.906	1.906	W-M	1.882	1.885	W-M	1.839	1.843	M
023	1.881	1.880	M	1.853	1.858	W-M	1.796	1.806)	M-S
221	1:864	1:865	M-S	1:839	1:844	M-S		1.801)	
213	1.746	1.743	VVW				1.688	1.690	VVW
301							1.677	1.681	VW
114	1.715	1.707)	S	1.690	1.689)	M-S	1.658	1.651	VW
131		1.713)			1.692)		1.636	1.638	M-S
310	1.688	1.685	VW-W				1.647	1.642	W-M
311	1.646	1.645	W	1.626	1.628	W-M	1.604	1.603	W
132	1.596	1.596	M-S	1.576	1.577	M	1.528	1.529	M
024	1.575	1.574	M	1.554	1.556	W-M	1,514	1.515	M
204	1.547	1.547	W	1.529	1.531	W-M	1.500	1.501)	S-VS
312	1.540	1.541	S-VS	1.522	1.525	S		1.500)	
105									
231		1.495	ov.(320)						
303									
321									
320	1.498	1.494	VVW						
223	1.534	1.533	W	1.514	1.516	VW-W	1.481	1.481	W
133	1.447	1.446	M-S	1.427	1.428	M-S	1.386	1.387	M-S
115	1.417	1.417	VW-W	1.401	1.402	VW-W	1.374	1.370	VW
313				1.387	1.389	VW			
040				1.373	1.380	W	1.331	1.332	VW-W
041	1.376	1.374	W-M	1.357	1.357	M	1.310	1.311	W
224	1.354	1.354	S	1.338	1.339	S	1.308	1.308	S-VS
025				1.322	1.323	W	1.288	1.290)	W
140					1.334	ov.(224)		1.290)	
400	1.325	1.326	W-M	1.310	1.314	M	1.294	1.295	W-M
215	1.285	1.286)	VVW	1.271	1.275)	VW	1.245	1.246)	VW
323		1.288)			1.274)			1.248)	
233					1.292)	VW		1.258	ov.(410)
042	1.313	1.312	VW	1.297	1.296)		1.251	1.253)	VVW
125								1.252)	
410							1.257	1.258	VW
142				1.256	1.258)	W		1.218	ov.(331)
411					1.258)		1.240	1.240	VW
330							1.238	1.238	VW
134								1.242	ov.(411)
006	1.271	1.270	W		1.257	ov.(411)	1.228	1.228	W
314	1.265	1.262)	M	1.250	1.249)	S	1.226	1.226	M-S
331		1.264)			1.250)		1.221	1.221)	W-M
402	1.256	1.252	VW	1.239	1.239	VVW		1.222)	
043	1.226	1.224	VW-W		1.209	ov.(412)		1.171	ov.(241)
240	1.238	1.236	VW	1.220	1.221	VW	1.184	1.185	W
412	1.222	1.222)	M-S	1.210	1.209	W			
241		1.220)		1.206	1.205	S	1.169	1.170	M-S
332	1.216	1.215	W-M	1.202	1.201	W-M	1.173	1.174	M-S
116	1.206	1.206	M-S	1.193	1.193	S-VS	1.166	1.166	S-VS
420	1.198	1.198	W	1.185	1.185	W	1.164	1.165	S-VS
225	1.195	1.195)	M	1.181	1.181	S	1.155	1.155	M-S
143		1.193)		1.177	1.178)	W			
234					1.177)				
421	1.183	1.183	W-M	1.170	1.170	S	1.150	1.150	M
324	1.177	1.176)	W-M	1.163	1.163)	M-S			
242		1.176)			1.162)				
026	1.152	1.156)	S						
413		1.150)							
305		1.154)							
135		1.153)							
206									
422									
333									
315									

Notes: (1.) VS = very strong, S = strong, M = medium, W = weak
(2.) ov. (hkl) = This line overlaps the (hkl) line,

Table 2. *Crystallographic data on the perovskite-like compounds*

Compound	a (Å)	b (Å)	c (Å)	Vol. per unit cell (Å^3)	X-ray density (g.cm.$^{-3}$)	Pseudo-cell dimensions a (= c) (Å)	b (Å)	β (°)
$GdFeO_3$	5·346	5·616	7·668	230·2	7·52	3·877	3·834	92·8
$EuFeO_3$	5·371	5·611	7·686	231·6	7·34	3·884	3·843	92·5
$SmFeO_3$	5·394	5·592	7·711	232·6	7·26	3·885	3·856	92·0
$NdFeO_3$	5·441	5·573	7·753	235·1	7·01	3·895	3·877	91·4
$PrFeO_3$	5·495	5·578	7·810	239·4	6·79	3·912	3·905	90·8
$LaFeO_3$	5·556	5·565	7·862	243·1	6·63	3·932	3·931	90·2
$YFeO_3$	5·302	5·589	7·622	225·9	5·67	3·852	3·811	93·0
$YCrO_3$	5·247	5·518	7·540	218·3	5·75	3·807	3·770	92·9
$YAlO_3$	5·179	5·329	7·370	203·4	5·35	3·716	3·685	91·6

The single-crystal photographs established the isomorphism of the $GdFeO_3$, $LaFeO_3$ and $YFeO_3$. Using the data obtained from the single-crystal photographs of the $GdFeO_3$, the powder photograph of the $GdFeO_3$ was indexed and subsequently it was found possible to index all the lines on the powder photographs of all the compounds. A comparison of intensities indicates also that the compounds are isostructural, but that there are differences in atomic coordinates from those in $GdFeO_3$.

The powder diffraction data for all the compounds are shown in Table 1.* All of the photographs have the same systematic absences, namely: reflections of the type ($h0l$) with ($h+l$) odd, and ($0kl$) with k odd. The probable space groups are either D_{2h}^{16}–$Pbnm$ or C_{2v}^{9}–Pbn. The structure of $GdFeO_3$ was solved on the basis of *Pbnm* as the most probable space group, but it was pointed out that the structure could not have a center of symmetry in the strictest sense because the iron sublattices in $GdFeO_3$ are imperfectly antiferromagnetic. This is probably also the case for all the orthoferrites reported here. (See also Gilleo, 1956*a*; Guiot-Guillain, 1953.)

The X-ray crystallographic data on these compounds are listed in Table 2.

Optical examination

Optical examination of the crystals of the various compounds confirmed the observation that the crystals are all orthorhombic. The gadolinium and yttrium orthoferrites are the most transparent of the orthoferrites, but crystals of these as thick as 0·1 mm. are opaque. By transmitted light, the orthoferrites are orange-brown; $YAlO_3$ is apparently colorless and $YCrO_3$ emerald green. By reflected light, the $GdFeO_3$ is very dark brown with adamantine luster; $EuFeO_3$ is very dark brown, adamantine to submetallic; $NdFeO_3$ is black, submetallic; $PrFeO_3$ and $LaFeO_3$ are black, submetallic to metallic; $YFeO_3$ is dark brown, adamantine; $YAlO_3$ is vitreous and pale brown, and $YCrO_3$ is vitreous and emerald green.

The major faces developed in these crystals are the {110} and {001}. These faces are parallel to the faces of the perovskite-like pseudo-cell (see Fig. 1). Three types of twinning were observed: (1) twin plane {112} of somewhat complicated nature as shown in detail in Fig. 2; (2) twin plane and composition plane {110}*; (3) $PrFeO_3$ particularly showed twinning on {011} of the type which would be known as penetration spinel twinning if the crystal were cubic. (The {011} plane is the {111} plane of the pseudo-cell.)

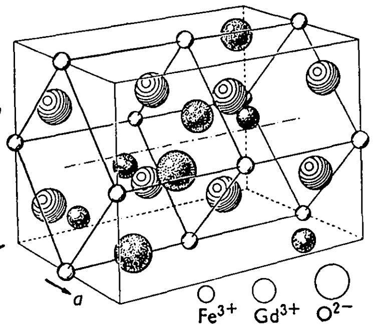

Fig. 1. The unit cell of $GdFeO_3$ showing the perovskite-like monoclinic pseudo-cell. The large stippled circles represent oxygen ions in fourfold positions; the other large circles represent oxygen ions in eightfold positions.

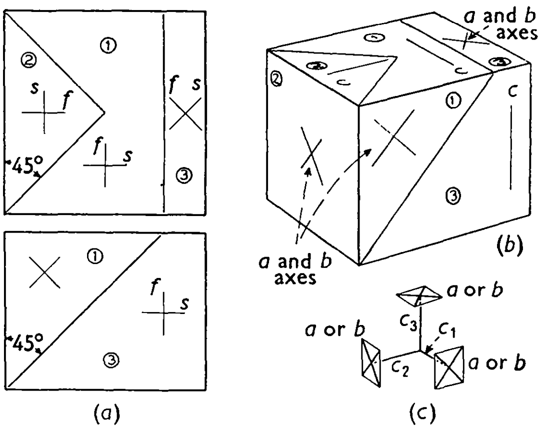

Fig. 2. Crystal of $YAlO_3$, twinned on {112}.

The best crystals for optical examination were those

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* Only observed reflections are listed.

* Twinning on the {110} plane was indicated also by the single-crystal photographs discussed earlier.

of $YAlO_3$, which were studied in most detail for twinning. In most cases of the first type of twinning in these crystals {112} is the composition plane as well as the twin plane, but not always, as shown in Fig. 2. In this type of twinning in $PrFeO_3$, the composition plane shows a linear trace which is not in all cases parallel or at 45° to the crystal edge. Crystals of $LaFeO_3$, which in this group of compounds shows least distortion from the ideal perovskite* (though the distortion is nevertheless still substantial, as will be shown later), show quite irregular twin boundaries.

The indices of refraction for $YAlO_3$, $YCrO_3$ and $GdFeO_3$ are greater than 1·64. The indices for the less translucent crystals could not be reliably checked but they are most probably also high. None of the crystals was found to be pleochroic.

Discussion

The $GdFeO_3$ structure parameters are reproduced in Table 3 and diagrams of the structure are given in Figs. 1 and 3. In Fig. 1, the orthorhombic unit cell is shown and the monoclinic pseudo-cell is outlined. Fig. 3(*a*) is an orthogonal projection of the structure on to the (001) plane. Figs. 3(*b*) and (*c*) are orthogonal projections of quarter-parts of the unit cell on to the (001) plane. The two quarter-parts chosen lie one above the other in the *c* direction, as indicated by the *z* coordinates of the atoms. If the structure were the so-called 'ideal perovskite structure', these two parts would be cubes with gadolinium ions at the corners, oxygens at the face-centers and iron at the body-centered position. They would project on to a single square with iron at the center.

Table 3. *Coordinates of ions in* $GdFeO_3$

Ion	Position	*x*	*y*	*z*
Gd^{3+}	4(*c*)	−0·018	0·060	$\frac{1}{4}$
Fe^{3+}	4(*b*)	$\frac{1}{2}$	0	0
O_I^{2-}	4(*c*)	0·05	0·47	$\frac{1}{4}$
O_{II}^{2-}	8(*d*)	−0·29	$0{\cdot}27_5$	0·05

Comparing Fig. 3 with this ideal arrangement, we see that each 'face-centered' oxygen is most closely bonded to two corner gadolinium ions. In spite of the appreciable departure of the oxygens from the face-centered positions, two of the octahedral Fe^{3+}–O^{2-} bond angles are close to 90°. Referring to the lettered atoms in Fig. 3(*a*) and (*c*), these angles are approximately 89° for O_A^{2-}–Fe^{3+}–O_C^{2-}, 91° for O_B^{2-}–Fe^{3+}–O_C^{2-} and 83° for O_A^{2-}–Fe^{3+}–O_B^{2-}.

The arrangement of the oxygen octahedra in these compounds, viewed along the *b* axis, is shown in Fig. 4.

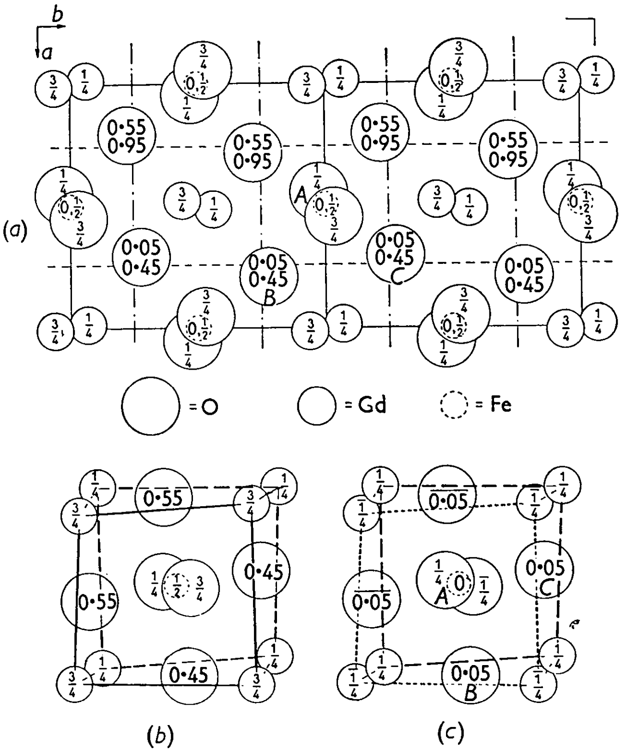

Fig. 3. (*a*) Orthogonal projection of two unit cells of $GdFeO_3$ on to the (001) plane.

(*b*) One-fourth part of the $GdFeO_3$ unit cell, rotated 45° with respect to (*a*) to show the 'distorted perovskite-like pseudo-cell'; orthogonal projection on to (001).

(*c*) One-fourth part of the $GdFeO_3$ unit cell from directly below part (*a*), similarly projected.

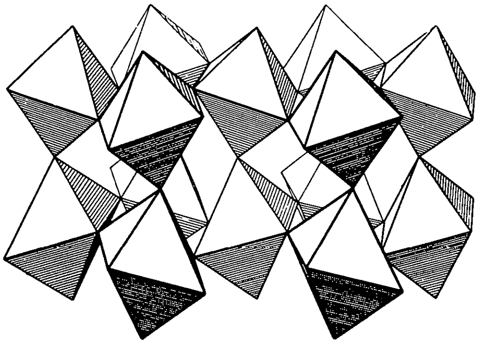

Fig. 4. The distorted oxygen octahedra in $GdFeO_3$, perspective view approximately along the *b* axis. The oxygens are located at the corners of the distorted, corner-linked octahedra. (The Gd and Fe ions are omitted from this diagram.)

The iron and gadolinium ions have been omitted to give an unobstructed view of the distorted octahedra. Unlike the structure proposed by Náray-Szabó, all the octahedra are related to a single one through the symmetry operations. In a single 'level' of octahedra, the octahedra are tilted toward or away from each other in planes containing neighboring edges. Octahedra in neighboring levels have faces tilted toward or away from each other.

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* 'Ideal perovskite' is taken here to be exemplified by cubic $BaTiO_3$ rather than by the original perovskite, $CaTiO_3$, which has not been found to exist in the phase with the ideal structure.

It is probable that the atomic positions gradually change from compound to compound toward those of the ideal perovskite structure as the relative ionic sizes become favorable. Because the intensity estimation of the lines on the powder photographs is rather inaccurate,* this gradual change is only apparent on close examination, but the difference between the $LaFeO_3$ and $GdFeO_3$ powder patterns is quite striking, as would be expected. The difference in the two is of course indicated much more vividly by the single-crystal photographs. For example, in $GdFeO_3$, the distribution of intensities is about the same in odd- and even-numbered layers taken with the *c* axis as rotation axis, whereas the odd-numbered layers of $LaFeO_3$ are much weaker than the even-numbered ones. However, the approach to the ideal perovskite by $LaFeO_3$ is not as close as one might be tempted to guess on examination of Table 2, which shows the pseudo-cell of $LaFeO_3$ to have very nearly cubic dimensions. An examination of the single-crystal photographs as well as the powder photographs indicates that the deviation from ideal is still substantial. Note, for example, (Table 1) the intensities of lines with odd *l*. These should approach zero as the structure approaches the ideal monomolecular unit. Some work by Gilleo (1956*b*) indicates the displacement of ions from ideal positions is substantial in $La(Co_{0.2}Mn_{0.8})O_3$, which is isostructural with the compounds discussed here, even though the pseudo-cell has a β angle very near 90°, as in $LaFeO_3$.

The results of work at higher temperatures give another indication of the magnitude of the deviation from ideal. A search was made for a transition in $GdFeO_3$ and $LaFeO_3$, using a high-temperature X-ray powder diffraction camera with 114·6 mm. diameter designed and built by W. L. Bond of these Laboratories. If the $LaFeO_3$ were really very close to the ideal structure, one might expect a relatively low transition temperature. However, no transition of $LaFeO_3$ was observed up to 845° C. The $GdFeO_3$ was taken to only 700° C. and no transition was observed. In both cases, however, there seemed to be an 'almost isotropic' expansion; that is, the expansion occurred in such a way that no lines of the powder photographs coalesced or were permuted relative to their positions in the room-temperature photographs. The photographs indicated that between 25 and 845° C. the $LaFeO_3$ lattice constants increased about 1%.

Subsequently, P. D. Garn of these Laboratories ran differential thermal analyses (Garn & Flaschen, 1956) on samples of $PrFeO_3$ and $LaFeO_3$. He found no transitions in $PrFeO_3$ up to 1100° C. and one in $LaFeO_3$ at 980° C. Further high-temperature X-ray work is contemplated and Garn is planning further differential analyses of other compounds in this group.

A powdered sample of $LaFeO_3$ was subjected to 100,000 lb.in.$^{-2}$ hydrostatic pressure at 275° C. for 24 hr. by O. L. Anderson of these Laboratories. The sample was removed and as rapidly as possible examined with the Norelco diffractometer. If a transformation did occur, it did not give rise to a metastable phase, i.e., the normal orthorhombic phase was observed.

The relationship among the lattice constants of the orthoferrites is shown in Table 2. The length of the *b* axis changes very little in the series of seven compounds. The difference between the *b* axis of the La compound and that of Gd compound (the maximum difference) is 0·051 Å. The *a* and *c* axes, however, increase gradually from $GdFeO_3$ to $LaFeO_3$, the absolute increments (in Å) being very nearly equal for the two axes for a given compound. With increase in the size of the *A* ion, both the *a* and *c* axes increase in length in such a way that half the diagonal of the (001) face (which is the direction of the *a* or *c* axis of the pseudo-cell—see Table 2) approaches half the length of the *c* axis (which is colinear with the *b* axis of the pseudo-cell). The ions apparently shift in such a way with these increases in lattice constants as to approach the ideal perovskite structure.

In these perovskite-like compounds there are four formula units in the unit cell or one in the asymmetric unit. It then follows that one may assign one quarter of the volume of the orthorhombic cell to one formula unit, and therefore derive the minimum average interionic distances in the structure.

The positions of the ions are such that departure from the idealized structure by lengthening of interionic distances is usually compensated by shortening of others. For example, the departure of the *x* and *y* parameters from the ideal values produces little change in the average length of the A–O_I bonds.

In $GdFeO_3$, if one takes the cube root of the volume of the pseudo-cell as the cell edge of the cube of a theoretical ideal perovskite $GdFeO_3$, the Gd^{3+}–O^{2-} and Fe^{3+}–O^{2-} distances in the idealized structure would be very nearly equal to the average distances (counting the very long ones—see Geller, 1956) in the true crystal. If this method of estimation of average distances is used for all the crystals discussed herein,

Table 4. *Theoretical cell sizes and interionic distances of idealized perovskite ABO_3 crystals*

		Distances (Å)	
Compound	a_0 (Å)	A^{3+}–O^{2-}	B^{3+}–O^{2-}
$GdFeO_3$	3·860	2·729	1·930
$EuFeO_3$	3·869	2·736	1·935
$SmFeO_3$	3·874	2·739	1·937
$NdFeO_3$	3·889	2·750	1·945
$PrFeO_3$	3·909	2·763	1·954
$LaFeO_3$	3·932	2·780	1·966
$YFeO_3$	3·837	2·713	1·919
$YCrO_3$	3·793	2·682	1·897
$YAlO_3$	3·705	2·620	1·853

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* One must consider also that the anomalous scattering of Cr radiation by the rare earths could have considerable effects on the intensities.

one sees from the results in Table 4 that in the orthoferrites there is a maximum difference in the Fe^{3+}–O^{2-} distance of 0·05 Å. We see that in the orthoferrites, the variation of the Fe^{3+}–O^{2-} distance in the theoretical structures is appreciable and one must therefore conclude that although the coordination is the same in all the compounds, the radii of the two ions are not—or perhaps another way of putting it is that other factors than the steric one must be considered. A similar argument may be made concerning the Y^{3+}–O^{2-} distances in the yttrium compounds for which there is a maximum difference of 0·09 Å. In attempting to attain the ideal perovskite structure, one must therefore consider the ion–ion interactions aside from or in addition to the steric factor, which is the only one implied in the Goldschmidt tolerance factor. However, it is known that in a given ABO_3 series (i.e., either A or B constant), use of a self-consistent set of radii in the tolerance factor does enable one to predict approach to the ideal structure.

Three of the compounds discussed here have been investigated earlier by other authors. These are $LaFeO_3$ (Náray-Szabó, 1947; Goldschmidt, 1926; Roth, 1954; Yakel, 1955), $YAlO_3$ (Náray-Szabó, 1947; Goldschmidt, 1926) and $YCrO_3$ (Katz, 1955; Looby & Katz, 1954). Náray-Szabó reported that $LaFeO_3$ is cubic with cell edge 3·89, probably kX. This is 0·03 Å shorter than half the c axis (or half the (001) pinacoid diagonal) of the $LaFeO_3$ reported here (Table 2). Roth and Yakel both call the compound cubic with cell edges 7·86 and 7·85 Å, respectively. These are very close to the c-axis (approximately equal to the (001) pinacoid diagonal) length reported here. The powder photograph of $LaFeO_3$ can very nearly be indexed on such a cell, but, as stated earlier, single-crystal data and optical examination establish the isomorphism of $LaFeO_3$ with $GdFeO_3$.

Náray-Szabó reported that $YAlO_3$ is monoclinic with $a = b = c = 7{\cdot}34$, probably kX., and $\beta \sim 90°$. In this case, it is quite probable that Náray-Szabó chose the B-centered monoclinic cell. If this is so, the actual lattice constants of this monoclinic cell should be $a = c = 7{\cdot}432$, $b = 7{\cdot}370$ Å and $\beta = 91{\cdot}6°$.

The compound $YCrO_3$ was first reported by Looby & Katz (1954). These authors indexed their powder pattern on a monoclinic cell with $a = c = 7{\cdot}61$, $b = 7{\cdot}54$ Å. An examination of the diffraction data indicated that lines were present for which $(h+l)$ is odd. This would rule out the possibility of end-centering. However, it turned out that all such reflections could be accounted for by Cr_2O_3 impurity. When these lines were omitted, as well as the two first very very weak lines which could not be accounted for by either Y_2O_3 or Cr_2O_3, and the proper transformation was applied, an orthorhombic cell with $Pbnm$ space-group absences was obtained. The cell edges of this cell are $a = 5{\cdot}238$, $b = 5{\cdot}518$, $c = 7{\cdot}54$ Å. Remeika (1956) prepared pure $YCrO_3$, the powder photograph of which did not show the Cr_2O_3 or other impurity lines appearing in Katz's film. The diffraction data for $YCrO_3$ are listed in Table 1 and the lattice constants in Table 2. The b and c axes of our $YCrO_3$ check Katz's exactly (as does the pseudo-cell angle); the a axes differ by about 0·01 Å.

Further work is contemplated on related compounds. Crystals of several additional aluminates, orthochromites, scandates, galliates and cobaltiates have already been prepared by J. P. Remeika and the X-ray investigation of these compounds is currently under way.

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