

## Lattice Constants of Orthoferrites\*†

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(Received 22 December 1964)

The lattice parameters of the orthoferrites  $R\text{FeO}_3$  where R is Y or one of the trivalent rare earth ions Tb, Dy, Ho, Er, Tm, Yb and Lu, are calculated by Cohen's analytical method. The parameters,  $a$  and  $c$ , vary regularly with the atomic number (or the ionic radius) of R; however the  $b$  parameter remains almost constant.

The lattice constants of the rare earth orthoferrites with chemical formula  $R\text{FeO}_3$ , where R is Y, Tb, Dy, Ho, Er, Tm, Yb and Lu, were calculated from X-ray powder data.

The materials employed in this work were prepared by the ceramic method from the oxides  $R_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  of a purity of 99.9% or better. The oxides were heated in a furnace to 1380–1420 °C for 16 hours in air.

The X-ray powder photographs were taken with a Norelco Straumanis camera with a diameter of 114.6 mm and cobalt radiation filtered through an iron foil. The powder photographs were indexed on the basis of the orthorhombic cell (Geller & Wood, 1956; Geller, 1956; Wold & Croft, 1959), Geller's (1958)  $\text{YFeO}_3$  crystallographic constants being used. No additional lines were observed, indicating that the reaction between the oxides  $R_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  had gone to completion and that all the compounds have the same space group as  $\text{YFeO}_3$ ,  $Pbnm (D_{2h}^{16})$  (Geller & Wood, 1956; Geller 1958; Coppens & Eibschütz, 1965).

\* The research reported in this document has been sponsored in part by the Air Force Materials Laboratory Research and Technology Division AFSC through the European Office of Aerospace Research, United States Air Force.

† Part of this work was done in partial fulfilment of the Ph. D. requirements of the author.

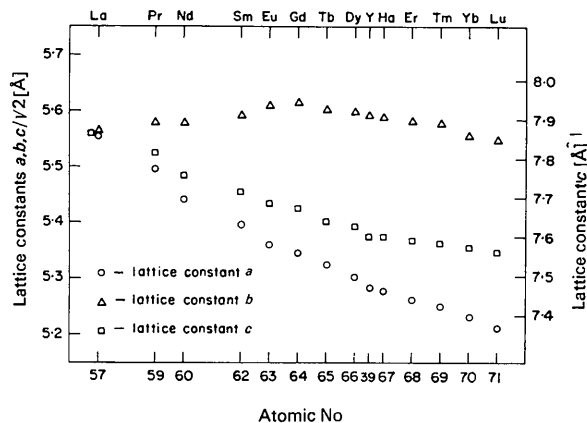


Fig. 1. Lattice constants  $a$ ,  $b$ ,  $c$  and  $c/2$  versus atomic number for the rare earth orthoferrites. (The values for La to Gd are taken from Geller & Wood, 1956).

Accurate lattice constants were calculated from 30 back reflexions only, by Cohen's (1935) analytical least-squares method. A least-squares program for the computer Control Data Corporation 1604 was written for this purpose.

The powder diffraction data for all the compounds are listed in Table 1. The crystallographic constants on

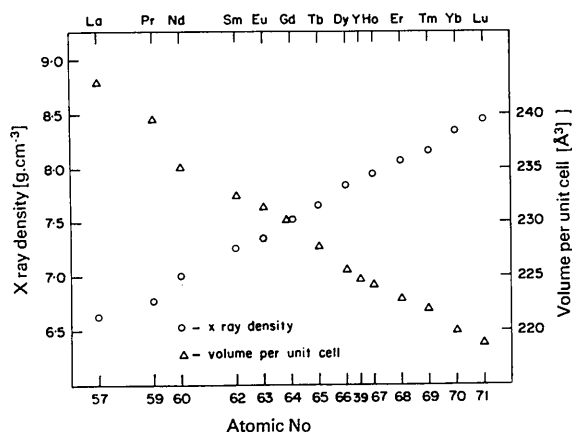


Fig. 2. Volume per unit cell and X-ray density versus atomic number for the rare earth orthoferrites. (The values for La to Gd are taken from Geller & Wood, 1956).

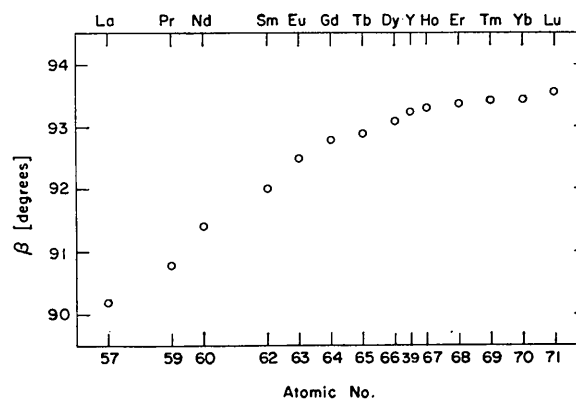


Fig. 3. Angle versus atomic number for the rare earth orthoferrites. (The value for La to Gd are taken from Geller & Wood, 1956).

these orthoferrites are listed in Table 2. The standard deviations of each lattice constant are  $\pm 0.003 \text{ \AA}$ . The calculated data for  $\text{DyFeO}_3$  are in good agreement with those obtained by Dalziel & Welch (1960).

The results are plotted in Fig. 1, together with those given by Geller for the first half of the series (Geller & Wood, 1956; Geller, 1956). Both Table 2 and Fig. 1 show a continuous decrease in lattice constants  $a$  and  $c$ , with increasing atomic number of R while  $b$  remains

essentially constant. The variations of volume of the unit cell and the density are shown in Fig. 2.

The perovskite-like pseudocell is almost cubic in  $\text{LaFeO}_3$ , as follows from the near equality of  $a$ ,  $b$  and  $c/\sqrt{2}$  and the  $\beta$  angle of  $90.2^\circ$ . Deviations from cubic symmetry increase with increasing atomic number as a result of the observed decrease of  $a$  and  $c$  but not of  $b$ , in this direction. The angle also increases in this direction (Fig. 3). The same type of regularity has been

Table 1. Powder diffraction data for orthoferrites  $\text{RFeO}_3$

R	Tb		Dy		Y		Ho		Er		Tm		Yb		Lu										
	hkl	$d_{\text{Obs}}$	$d_{\text{Calc}}$	I	$d_{\text{Obs}}$	$d_{\text{Calc}}$	I	$d_{\text{Obs}}$	$d_{\text{Calc}}$	I	$d_{\text{Obs}}$	$d_{\text{Calc}}$	I	$d_{\text{Obs}}$	$d_{\text{Calc}}$	I									
110	3.846	3.860	VS	3.828	3.849	VS	3.827	3.840	W-M	3.836	3.838	S	3.820	3.829	S	3.801	3.822	S	3.787	3.809	VS	{ 3.776	{ 3.783	S	
002	3.801	3.818	S	3.790	3.812	S	3.790	3.802	W-M	3.792	3.801	S-M	3.786	3.795	M-S	3.768	3.792	M	3.771	3.785	S	3.776	{ 3.783	S	
111	3.429	3.445	VS	3.412	3.436	VS	3.417	3.428	S	3.390	3.426	S	3.402	3.419	S	3.395	3.414	S	3.390	3.403	VS	3.381	{ 3.395	S	
020	2.790	2.801	S	2.785	2.799	S	2.786	2.796	S	2.769	2.796	S	2.790	2.791	M	2.776	2.788	S	2.768	2.779	S	2.767	{ 2.774	M	
112	2.707	2.714	VVS	2.693	2.708	VVS	2.692	2.702	VVS	2.680	2.701	VVS	2.699	2.696	VVS	2.682	2.692	VVS	2.674	2.685	VVS	2.673	{ 2.680	VVS	
200	2.656	2.663	S	2.634	2.651	S	2.633	2.642	S	2.626	2.639	S	2.629	2.632	S	2.619	2.626	S	2.619	2.626	S	2.603	{ 2.616	S	
021	2.623	2.630	M-S	2.612	2.627	S	2.616	2.624	M-S	2.610	2.624	M-S	2.621	2.620	S	2.609	2.617	S	2.609	2.617	S	2.603	{ 2.616	S	
211	2.290	2.294	M	2.274	2.286	M	2.271	2.279	M	2.262	2.277	M	2.265	2.271	W	2.259	2.267	M	2.250	2.259	W-M	2.245	{ 2.252	W	
022	2.254	2.258	M	2.244	2.256	M	2.246	2.252	W-M	2.237	2.252	M	2.245	2.249	W-M	2.240	2.246	M	2.233	2.240	W-M	2.229	{ 2.237	W	
202	2.180	2.184	S	2.164	2.176	S	2.162	2.169	M-S	2.158	2.168	S	2.156	2.163	M-S	2.152	2.159	S	2.144	2.152	S	2.138	{ 2.146	M	
113	2.121	2.125	M-S	2.111	2.121	M-S	2.133	2.115	M-S	2.104	2.115	M-S	2.102	2.110	M	2.105	2.109	M-S	2.100	2.104	M	2.095	{ 2.101	M	
272	0.733	0.739	VW	0.730	0.736	VW	0.727	0.733	VW	0.724	0.730	VW	0.721	0.727	VW	0.718	0.724	VW	0.715	0.721	VW	0.712	{ 0.718	VW	
212	2.0344	2.0349	VW	2.025	2.028	VW	2.016	2.022	VW	2.011	2.021	VW	2.013	2.017	VW	2.009	2.013	VW	2.004	2.007	VW	2.000	{ 2.005	VW	
220	1.925	1.930	VS	1.918	1.925	S	1.916	1.920	S	1.915	1.919	S	1.911	1.915	S	1.908	1.911	S	1.900	1.905	S	1.914	{ 1.899	M-S	
004	1.906	1.909	S	1.898	1.906	S	1.898	1.901	S	1.896	1.901	M	1.896	1.898	S	1.894	1.896	S	1.886	1.893	S	1.887	{ 1.891	M-S	
023	1.879	1.884	M-S	1.875	1.881	M-S	1.875	1.877	M	1.874	1.877	M	1.874	1.876	M-S	1.869	1.873	M-S	1.863	1.868	M	1.862	{ 1.866	W-M	
221	1.867	1.871	S	1.861	1.866	S	1.860	1.862	M-S	1.855	1.861	M	1.852	1.856	S	1.848	1.853	S	1.842	1.847	S	1.840	{ 1.842	M-M	
213	1.744	1.748	W	1.735	1.743	VW	1.737	1.738	VW	1.729	1.737	VW	1.728	1.731	VW	1.721	1.726	VW	1.718	1.726	VW	1.718	{ 1.723	VW	
301	{ 1.729	{ 1.729		{ 1.721	{ 1.721		{ 1.715	{ 1.715		{ 1.714	{ 1.714		{ 1.709	{ 1.709		{ 1.706	{ 1.706		{ 1.697	{ 1.697		{ 1.694	{ 1.694	VS	
114	1.714	1.711	VS	1.709	1.708	VS	1.711	1.704	VS	1.704	1.703	VS	1.703	1.700	VS	1.705	1.699	VS	1.697	1.695	VS	1.694	{ 1.693	VS	
131	{ 1.717	{ 1.717		{ 1.715	{ 1.715		{ 1.713	{ 1.713		{ 1.712	{ 1.712		{ 1.707	{ 1.707		{ 1.701	{ 1.701		{ 1.696	{ 1.696		{ 1.693	{ 1.693	VS	
222	{ 1.722	{ 1.722		{ 1.718	{ 1.718		{ 1.714	{ 1.714		{ 1.713	{ 1.713		{ 1.709	{ 1.709		{ 1.707	{ 1.707		{ 1.702	{ 1.702		{ 1.695	{ 1.695	VS	
310	1.689	1.692	W	1.679	1.685	W	1.678	1.680	W	1.670	1.678	W	1.670	1.674	W	1.667	1.670	VW	1.661	1.664	W	1.657	{ 1.658	VW	
311	1.650	1.652	W	1.641	1.646	W	1.650	1.640	W	1.631	1.639	W	1.632	1.634	W	1.630	1.631	W-M	1.622	1.625	W	1.618	{ 1.617	W	
132	1.598	1.600	M	1.594	1.598	M	1.5953	1.5955	M	1.589	1.595	M	1.591	1.592	W-M	1.589	1.590	M	1.580	1.586	W	1.582	{ 1.583	W	
024	1.5774	1.5773	M-S	1.572	1.575	M-S	1.5715	1.5719	M-S	1.565	1.572	M	1.565	1.569	M	1.5672	1.5678	M-S	1.561	1.564	M	1.561	{ 1.563	M	
204	1.5524	1.5514	S		1.5424	1.5428	S			1.536	1.539	S			1.530	1.533	S			1.529	1.531	S		{ 1.531	S
312	1.5467	1.5472	VS	1.543	1.541	S	1.539	1.536	S	1.536	1.535	S	1.532	1.531	M-S	1.535	1.528	S	1.529	1.523	S	1.528	{ 1.519	M-S	
133	1.4487	1.4488	S	1.444	1.447	S	1.4437	1.4444	M-S	1.440	1.444	S	1.439	1.442	S	1.4395	1.4400	S	1.434	1.436	S	1.433	{ 1.436	S	
303	{ 1.4560	{ 1.4560		{ 1.451	{ 1.451		{ 1.446	{ 1.446		{ 1.445	{ 1.445		{ 1.442	{ 1.442		{ 1.4390	{ 1.4390		{ 1.436	{ 1.436		{ 1.431	{ 1.431	VS	
115	{ 1.4199	{ 1.4199		{ 1.418	{ 1.418		{ 1.414	{ 1.414		{ 1.413	{ 1.413		{ 1.4098	{ 1.4098	VW	{ 1.407	{ 1.407		{ 1.403	{ 1.403		{ 1.400	{ 1.400	VW	
232	1.4192	1.4193	VW	1.415	1.417	VW	1.411	1.414	VW	1.409	1.413	VW	1.407	1.410	VW	1.4085	1.4085	VW	1.4042	1.4039	VW	1.399	{ 1.386	VW	
313	1.4087	1.4092	VW							1.392	1.396	VW	1.3934	1.3934	VW	1.3882	1.3893	VW	1.382	1.383	VW	1.379	{ 1.386	VW	
322	1.3950	1.3957	VW	1.386	1.391	VW	1.385	1.387	VW	1.383	1.386	VW	1.381	1.383	VW	1.3801	1.3807	VW	1.375	1.376	VW		{ 1.376	VW	
041	1.3768	1.3775	M	1.374	1.376	M	1.3744	1.3749	W	1.374	1.374	W	1.370	1.373	W	1.3703	1.3710	M	1.3656	1.3666	W	1.3639	{ 1.3640	W	
140				{ 1.353	{ 1.353		{ 1.3515	{ 1.3515		{ 1.351	{ 1.351		{ 1.349	{ 1.349		{ 1.347	{ 1.347		{ 1.343	{ 1.343		{ 1.340	{ 1.340	M	
224	1.3574	1.3571	S	1.352	1.354	S	1.3512	1.3508	S	1.349	1.350	M-S	1.345	1.348	M-S	1.3460	1.3461	M-S	1.341	1.343	M-S	1.3398	{ 1.3402	M	
025	1.343	1.354	W	1.337	1.339	VW	1.3354	1.3358	VW	1.334	1.335	VW	1.330	1.334	VW	1.3335	1.3325	VW	1.328	1.329	VW	1.3273	{ 1.3282	VW	
400	1.3315	1.3315	W	1.324	1.326	W	1.3206	1.3208	W	1.3190	1.3195	W	1.313	1.316	W	1.3133	1.3128	VW	1.3077	1.3082	VW	1.3028	{ 1.3032	W	
042	1.309	1.315	VW	1.312	1.314	VW	1.3115	1.3121	VW													1.2753	{ 1.2749	VW	
323																						1.2719	{ 1.2716	VW	
006				1.2704	1.2705	W	1.2671	1.2672	W	1.2663	1.2670	W		1.265	W	1.262	1.264	VW	1.2614	1.2616	VW	1.259	{ 1.261	VW	
411				{ 1.2718	{ 1.2718		{ 1.2674	{ 1.2674		{ 1.2663	{ 1.2663			1.2627	1.2628									{ 1.260	
331		1.2687	M	1.2648	1.2653	M	1.2632	1.2623	M	1.2613	1.2616	M	1.2573	1.2580	M	1.2566	1.2566	W-M	1.2522	1.2524	M	1.2484	{ 1.2489	M	
314	1.2669	1.2663	S				1.2542	1.2586	W				1.2540	1.255	W	1.2538	1.2532	W							
402				1.2512	1.2519	VW				1.2462	1.2465	VW	1.2429	1.2432	VW	1.239	1.240	VW	1.2364	1.2365	VW				
043	1.2264	1.2270	W	1.2247	1.2258	W	1.2241	1.2241	W	1.2236	1.2239	VW	1.2215	1.2220	VW	1.219	1.221	VW	1.2178	1.2170	VW	1.2153	{ 1.2151	VW	
241	1.2229	1.2235	M	1.2206	1.2216	M	1.186																		

Table 1 (cont.)

hkl	d <sub>Obs</sub>	d <sub>Calc</sub>	I	d <sub>Obs</sub>	d <sub>Calc</sub>	I	d <sub>Obs</sub>	d <sub>Calc</sub>	I	d <sub>Obs</sub>	d <sub>Calc</sub>	I	d <sub>Obs</sub>	d <sub>Calc</sub>	I	d <sub>Obs</sub>	d <sub>Calc</sub>	I	d <sub>Obs</sub>	d <sub>Calc</sub>	I			
316	1.0176	{1.0171 VS		1.0145	{1.0145 VS		1.0110	{1.0116 VS		1.0107	{1.0111 VS		1.0086	{1.0092 S		1.0071	{1.0079 S		1.0052	1.0054 S		1.0030	1.0036 M-S	
145		{1.0175		{1.0142			{1.0102			{1.0100			{1.0084			{1.0073				1.0046			1.0032	
424		{1.0075					{1.0112			{1.0106			{1.0083			{1.0065				1.0031	1.0035 M		1.0005	1.0008 M
153	1.0070	1.0069		1.0059	1.0044		{1.0045 M-S		1.0034	1.0043		M	1.0034	{1.0027 M		1.0010	{1.0015 W-M		0.9988	{0.9984 W		0.9975	{0.9967 W	
343		{1.0094					{1.0051						{1.0027 M			{1.0012				{0.9981			{0.9967	
512	1.0098	{1.0092 S		1.0054	{1.0050 VS		1.0008	1.0015	S	1.0002	1.0007	S	0.9976	0.9980	S	0.9949	0.9958	M	0.9922	0.9925	M	0.9885	0.9890	
217				{0.9914									0.9866	0.9868	VW	0.9857	0.9857	W	0.9840	0.9836	W	0.9829	0.9825	
520	0.9956	0.9956	VW	0.9916	{0.9916								0.9810	0.9816	W	0.9805	0.9811	M	0.9790	0.9789	W	0.9776	0.9772	
415													0.9793	0.9793	M	0.9789	0.9789	M	0.9773	0.9770	M	0.9751	0.9757	
335	0.9843	0.9839	M	0.9818	0.9817	M	0.9793	{0.9793		0.9789	{0.9789		0.9773	{0.9767		0.9751	{0.9757		0.9728	0.9730	W	0.9711	0.9710	
521													0.9746			0.9710				0.9728	0.9730	W	0.9711	0.9710
503							0.9751	{0.9752		0.9741	{0.9744		0.9716	{0.9718	VW	0.9692	{0.9698	VW	0.9682	{0.9677	VW	0.9631	0.9635	
236				0.9766	0.9764	VW				0.9738			0.9722			0.9710				0.9687			0.9631	0.9635
326				0.9682	0.9680	VW				0.9652	0.9649	VW	0.9633	0.9631	VW	0.9613	0.9618	W	0.9597	0.9594	W	0.9574	0.9577	
513	0.9684	0.9678	W	0.9642	0.9640	VW	0.9602	0.9607	W	0.9606	0.9600	VW	0.9633	0.9631	VW	0.9613	0.9618	W	0.9597	0.9594	W	0.9574	0.9577	
440	0.9654	0.9650	M							0.9575			0.9575			0.9555				0.9555			0.9498	0.9497
745	0.9627	{0.9624 M-S		0.9607	{0.9609 M-S		0.9588	0.9589	M	0.9594	{0.9587 M-S		0.9572	{0.9571 M-S		0.9555	{0.9559 M-S		0.9532	{0.9533 M-S		0.9519	0.9517	
441	0.9574	0.9574	M-S	0.9545	0.9548	M-S	0.9523	0.9525	M	0.9524	0.9519	M	0.9502	0.9498	S	0.9476	0.9482	S	0.9451	0.9450	M	0.9426	0.9423	
008							0.9503	0.9504	W	0.9506	0.9503	W											0.9423	0.9423
344	0.9530	0.9528	W	0.9507	0.9508	W				0.9488			0.9466			0.9453	S		0.9424			0.9404		
154	0.9508	0.9507	M	0.9496	0.9497	M-S	0.9483	0.9483	M-S	0.9482	0.9481	M	0.9472	0.9466	M-S	0.9450	0.9455	M	0.9428	0.9427	M	0.9409	0.9412	
227	0.9493	0.9496	W	0.9476	0.9478	M	0.9454	0.9454	M	0.9451	0.9451	W	0.9440	0.9435	W	0.9423	0.9425	W	0.9405	0.9404	W	0.9392	0.9393	
350	0.9473	0.9475	W	0.9460	0.9458	M	0.9436	0.9441	W-M	0.9435	0.9437	W	0.9420	0.9419	W	0.9401	0.9405	W-M	0.9378	0.9373	W	0.9358	0.9351	
046										0.9389			0.9371	0.9373	W	0.9358	0.9364	W						
425	0.9453	0.9448	W-M	0.9421	0.9420	M	0.9390	0.9392	M	0.9378	0.9387	W	0.9366	0.9366	W	0.9346	0.9351	M	0.9323	0.9325	W	0.9301	0.9302	
351	0.9405	0.9403	M	0.9385	0.9386	M-S	0.9368	0.9369	M	0.9361	0.9365	M	0.9349	0.9347	M-S	0.9329	0.9337	M-S	0.9305	0.9302	M	0.9285	0.9280	
434										0.9374			0.9369			0.9349			0.9337			0.9305		
442	0.9360	0.9355	W	0.9331	0.9304	0.9308	VW	0.9297	0.9303	VW			0.9261	0.9267	VW									
060	0.9336	0.9337	VW	0.9332	0.9330	W	0.9320	0.9320	VW	0.9317	0.9318	VW	0.9302	0.9303	VW	0.9288	0.9293	VW	0.9256	0.9262	VW	0.9239	0.9245	
146		{0.9274		{0.9262			{0.9244			{0.9244			0.9225	{0.9224		0.9212	{0.9215		0.9195	{0.9194		0.9184	{0.9183	
137	0.9282	{0.9274 S		0.9261	{0.9261 S		0.9239	{0.9240 S		0.9235	{0.9238 S		0.9225	{0.9224 S		0.9212	{0.9215 S		0.9195	{0.9194 S		0.9184	{0.9184 S	
307		{0.9291		{0.9270			{0.9244			{0.9244			0.9225	{0.9224		0.9212	{0.9215		0.9195	{0.9194		0.9184	{0.9184 S	
118	0.9260	0.9265	M	0.9249	0.9249	S-M	0.9220	0.9225	M-S	0.9221	0.9224	M	0.9209	0.9210	M	0.9198	0.9201	W-M	0.9175	0.9183	M	0.9174	0.9176	
160													0.9154	0.9151	VW							0.9103	0.9103	
406	0.9204	0.9199	W	0.9173	0.9172	W				0.9139	0.9139	W	0.9120	0.9120	W	0.9100	0.9105	W	0.9079	0.9082	W			
531	0.9189	0.9185	M-S	0.9155	0.9153	S	0.9123	0.9126	M-S	0.9118	0.9119	W	0.9094	0.9096	W	0.9072	0.9078	W	0.9046	0.9047	W	0.9021	0.9017	
317	0.9169	0.9168	M	0.9146	0.9147	M-S	0.9121			0.9117			0.9101	0.9101	W	0.9087	0.9089	VW	0.9066	0.9068	W			
161													0.9095			0.9085								
514										0.9101	0.9105	W	0.9081	0.9082	W	0.9060	0.9065	W	0.9031	0.9037	VW	0.9008	0.9009	
062	0.9069	0.9069	M	0.9063	{0.9062 M-S		0.9052	{0.9054 M-S		0.9050	{0.9050 M		0.9039	{0.9036		0.9023	{0.9026 M-S		0.9001	{0.8996 W-M				
254		{0.9071		{0.9055			{0.9053			{0.9037			0.9027			0.8998								
336				0.9028	0.9005	M-S	0.9002			0.8996			0.8974			0.8974								
078	0.9034	0.9034	M	0.9021	0.9020	M-S	0.8999	0.8998	S	0.9002	0.8997	M-S	0.8987	0.8994	S	0.8973	0.8975	M-S						
443	0.9026	0.9023	S	0.9002	0.9000	S	0.8978	0.8978	S															
532	0.8993	0.8992	S																					

Table 2. Crystallographic constants of orthoferrites RFeO<sub>3</sub>

R	a(Å)	b(Å)	c(Å)	c/√2(Å)	Vol. per unit cell (Å <sup>3</sup> )	X-ray density (g/cm <sup>3</sup> )	Pseudo-cell dimensions		
							a' = c' (Å)	b' (Å)	β(°)
Tb	5.326	5.602	7.635	5.399	227.8	7.66	3.865	3.818	92.89
Dy	5.302	5.598	7.623	5.390	225.6	7.84	3.855	3.812	93.11
Y	5.283	5.592	7.603	5.376	224.6	5.70	3.846	3.802	93.25
Ho	5.278	5.591	7.602	5.375	224.3	7.96	3.844	3.801	93.3
Er	5.263	5.582	7.591	5.367	223.0	8.07	3.836	3.796	93.37
Tm	5.251	5.576	7.584	5.363	222.1	8.16	3.830	3.792	93.44
Yb	5.233	5.557	7.570	5.353	220.1	8.35	3.817	3.785	93.44
Lu	5.213	5.547	7.565	5.349	218.8	8.46	3.806	3.783	93.56

observed in other measurements of these compounds such as internal field (Eibschütz, Gorodetsky, Shtrikman & Treves, 1964), Curie temperature (Eibschütz *et al.*, 1964) and magnetization (Gorodetsky & Treves, 1965).

The data for YFeO<sub>3</sub> fall between those for DyFeO<sub>3</sub> and HoFeO<sub>3</sub> for all the lattice parameters, as well as for the internal field and Curie temperature. These observations are consistent with the fact that the ionic radius of Y falls between those of Dy and Ho.

The author wishes to thank Professor E. Banks, S. Shtrikman and Dr D. Treves for many critical discussions, Mrs T. Gilad for measuring the powder photo-

graphs and Professor E. H. Frei under whom this work was performed.

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